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Distribution of Thallium in Soil and Plants Growing in the Keban Mining District of Turkey and Determined by ICP-MS

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INTRODUCTION

With respect to degree of toxicity, Tl ranks alongside Pb, Hg, and Cd. Thallium is emitted into the environment due to lead, zinc, and similar mining activities. Studies with regard to Tl concentrations in environmental and plant samples are relatively new and rare (1). Plants may also serve as biomonitors of anthropogenic contaminants. Since Tl is a highly toxic element, it has caused a number of outbreaks of poisoning around the world, even resulting in high mortalities (2–3). Therefore, all data relating to Tl concentrations in the environment are of significant importance. To this effect, a detailed environmental Health Criteria monograph on Tl was published by the World Health Organization - International Program on Chemical Safety in 1996 (4).

Thallium is present in the environment as a result of natural processes and from anthropogenic sources. It is emitted into the environment from the mining processes of sulphide ores containing heavy metals (in particular lead, zinc, and copper) as well as from industrial sources such as coal-burning power plants, brick works and cement plants, combustion of fossil fuels, oil refining, and metal smelting (4).

Thallium is also used in small quantities in the electronics industry, the production of certain glasses and crystals, and in the manufacture of medical diagnostics

ABSTRACT

In this study, we examined the Tl concentrations in soil and plants taken from an abandoned Pb-Zn-Cu mining area (Keban, Turkey). This region contains Pb, Zn, and Ag sulphide mineralizations that have been mined for 6000 years. For this purpose, soil and plant parts (including roots and shoots) were taken from 20 points in that area and the Tl concentrations determined by ICP-MS. The plants *Euphorbia macroclada*, *Verbascum cheiranthifolium* Boiss, and *Astragalus gummifer* were examined. The Tl levels in the soils ranged from 3.0–27.6 mg kg⁻¹ which is 3–27 times higher than in uncontaminated soils (1.0 mg kg⁻¹). The observed Tl levels in plant parts ranged from 0.05–4.62 mg kg⁻¹ which is up to 92-times higher than the allowable levels (0.05 mg kg⁻¹) proposed in the literature. It was also observed that high concentrations of metals such as Mo, Cu, Pb, Zn, Ag, and As inhibit the Tl uptake by plant roots and shoots.

tools such as scintigraphy. In the past, Tl has commonly been used as a rodenticide, but its use for this purpose has been banned in many countries (4–7).

The concentration of thallium (5) in plants (shoots and roots) from the calamine waste heap was found 100–1000 times higher than the level normally found in plants [0.05 mg/kg Tl dry wt (8)]. Furthermore, an average concentration of thallium of geological origin of 1.54 mg/kg dry wt (with a maximum value of 55 mg/kg) has been

reported for soil (6). Tremel et al. found that rape seeds (*Brassica napus*) contained the largest amounts of thallium, up to 33 mg/kg dry wt (shoots, up to 20 mg/kg dry wt) (7).

In China (2004), thallium contents ranged from 40 to 124 mg/kg in soils originating from the Tl-Hg-As mineralized area; from 20 to 28 mg/kg in slope wash materials; from 14 to 62 mg/kg in alluvial deposits downstream; from 1.5 to 6.9 mg/kg in undisturbed natural soils; and from <0.2 to 0.5 mg/kg Tl in soils in the background area (9). In 1981, emissions from a cement plant in Germany led to high Tl concentrations in soils, river sediments, brooks, and in garden vegetables (10). Several recent studies report on the relationship between Tl concentrations in environmental samples such as soil, water and plant, and their possible health effects (5,11–13). These studies also point out that more research is required to investigate the accurate concentration of Tl in all environmental and biological samples.

Thallium concentrations in uncontaminated areas have been found to range from 0.01 to 1.0 mg kg⁻¹ (ppm) for soil, less than 1 ng mL⁻¹ (ppb) for water, and below 0.1 mg kg⁻¹ for plants (dry weight) (14). Concentrations exceeding 1 mg kg⁻¹ in soil (basis on dry weight) are usually indicative of an anthropogenic source. On the other hand, much higher values have been found in the vicinity of some metallic ore deposits, metal works, and a surrounding cement plant (5,9–10,15–17). Thallium occurrence and its effects

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on plants were reviewed in detail by Heim et al. (18). They found that the median top-soil content is 0.5 mg/kg in the area investigated, and the moss *Pleurozium schreberi* grown in this area contains 0.04–0.13 mg/kg and the moss *Polytrichum formosum* between 0.01 and 0.05 mg/kg Tl.

The most common techniques for the determination of Tl at very low levels are flameless atomic absorption spectroscopy (flameless AAS) (5–7), inductively coupled plasma optical emission spectroscopy (ICP-OES) (18), inductively coupled plasma mass spectrometry (ICP-MS) (15,19), voltammetry (20), and X-Ray fluorimetry (21).

In this study, Tl concentrations were determined by ICP-MS in top-soil samples, the roots and shoots of the plants, including *Euphorbia macroclada*, *Verbascum cheiranthifolium* Boiss, and *Astragalus gummife*, all found in the Keban mining area. The results were compared in order to investigate the correlation between the soil and the root and shoots of the plants growing there.

EXPERIMENTAL

Instrumentation

A PerkinElmer SCIEX ELAN® 9000 inductively coupled plasma mass spectrometer was used for the determination of uranium and thallium (PerkinElmer SCIEX, Concord, Ontario, Canada). The operating conditions as recommended by the manufacturers (23) are given in Table I.

The Study Area

In this study, the plants and associated soil samples were collected from an area consisting of granitic-syenitic rocks in the Keban mining district (Elazig, Eastern Turkey) (Figure 1). This area has a Pb-Zn mining history going back

6000 years and is heavily contaminated with toxic metals such as Pb and As due to ancient and modern mining activities.

Plant Samples

The vegetation in the investigated area is very poor and only a few annual and biannual plant species are scattered on an otherwise barren rocky landscape. The plant species found in the Keban region are able to grow in severe climate conditions because of their massive

and deep-reaching root systems and their ability to live in areas not enriched with organic material. Briefly, *Euphorbia macroclada* Boiss (local name: Sütlegen), *Verbascum cheiranthifolium* Boiss (local name: Sigr Kuyruğu), and *Astragalus gummifer* (local name: Keven) are among the plant species examined for this study. Their ability to live in heavily contaminated areas and their deep-reaching root systems were the criteria for choosing the plants.

TABLE I
Operating Conditions for ICP-MS

Inductively coupled plasma	PerkinElmer SCIEX ELAN 9000 ICP-MS
Nebulizer	Cross-flow
Spray chamber	Ryton®, double pass
RF power	1000 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	1.0 L min ⁻¹
Carrier gas flow rate	0.9 L min ⁻¹
Sample uptake rate	1.0 mL min ⁻¹
Detector mode	Auto

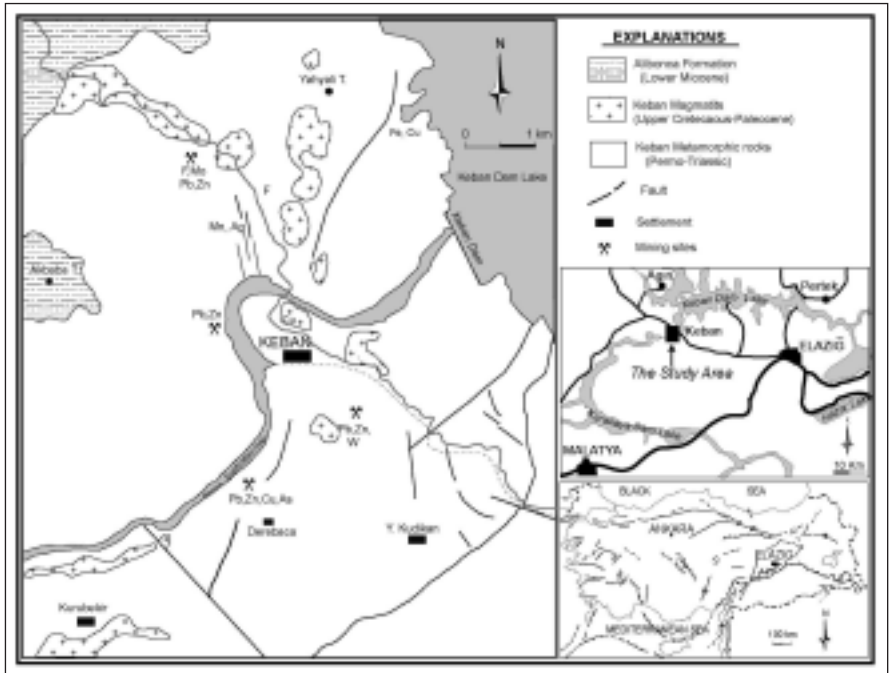


Fig. 1. Geological map of the study area (simplified from Akgul (23)).

Preparation of Samples

The plant samples (including the root) and surrounding soil were taken from 20 sites of the Keban mining area in Elazig, Turkey.

Plant Samples

The plant samples were collected randomly, and the collection sites selected represented the whole of the Keban mining area. Triplicate shoot and root samples were taken from each sampling site. The root samples were taken from a depth of 30–40 cm. The shoot and root samples of the studied plants were thoroughly washed with tap water followed by distilled water and dried at 100 °C in an oven for 30 minutes, then at 60 °C for 24 hours. The plant samples were ashed by heating in a furnace at 250 °C for about 30 minutes; then the heat was gradually increased to 500 °C for 2 hours. These ashed samples (1.00–3.00 g) were ground with hand mortars, then labeled, and analyzed by ICP-MS at ACME Analytical Labs in Canada using the parameters listed in Table I.

For digestion of the ashed samples, concentrated HNO₃ was added (2 mL was used for 1.0 g) to each sample and heated on a hot plate below 95 °C for one hour. The mixture of HCl-HNO₃-H₂O (1/1/1) was then added and further heated on a hot plate for one hour at 95 °C by stirring occasionally (6 mL of the mixture at a ratio of 1/1/1 was used for 1.0 g). The ratio of the ashed Tl samples to dry samples was found to be as follows: *Euphorbia*: 42%, *Verbascum*: 44%, *Astragalus*: 44 % at the studied conditions described below. Thus, the metal concentrations on a dried-weight basis were calculated from the concentrations on ashed-weight basis.

Soil Samples

Triplicate soil samples (1.0 g) were collected from 30–40 cm

depths in the area surrounding the roots. For digestion of the soil samples, HCl-HNO₃-H₂O was added (6 mL of the mixture at a ratio of 1/1/1 for 1.0 g) and heated on a hot plate for one hour at 95 °C. Thus, all sample constituents, except the silicates, were digested.

RESULTS AND DISCUSSION

Accuracy of the method was studied by examining the shoots of various samples found in the area, including EU-21, VR-25, and AS-28, and the soil samples associated with these samples by an independent analytical method. The instrument used was a PerkinElmer Model 3100 Optima DV inductively coupled plasma optical emission spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) following the parameters as described in the manufacturer's manual. It was observed that the recoveries were at least 90% for all studied samples.

With respect to degree of toxicity, Tl ranks with Pb, Hg, and Cd, but Tl is even more toxic than these metals (2,3,5,24). It is known that the Tl content in soils depends on their geological composition and the anthropogenic contaminants. Tremel et al. (6–7) studied the uptake of Tl and its accumulation in several species of crop plants grown in soils with high Tl levels of geochemical origin. They found that *Brassica napus* (rape seeds) contained the largest amounts of Tl up to 20 mg kg⁻¹ dry weight for shoots (6–7).

Our study revealed that the largest amount of Tl was accumulated in *Euphorbia*, but this accu-

mulation depends on the other metal concentrations in the soil and root. The obtained results for all studied soil samples were found to be 3–27 times greater (Table II – see next page) than the Tl concentrations in uncontaminated soils as reported by Smith and Carson (13). This can be attributed to the presence in that area of sulphide ores containing lead, zinc, silver, and CaF₂. The correlation between the levels of other elements and Tl are given in Table III. It can be seen that there are significant positive correlations between Tl and Mo, Cu, Pb, Zn, Ag, and As. In addition, Tl concentrations of the studied plants were found to be 143 times (14.3 mg kg⁻¹) greater than the Tl concentrations (0.1 mg kg⁻¹) of plants grown in uncontaminated areas.

Tl in *Euphorbia*

The number such as -44, -21, -25, -28 in Table II signifies the point where plant and soil samples were collected. For example EU-44 means that the *Euphorbia* plant was taken from the point number -44.

Table II (see next page) shows that the Tl concentrations in both shoot and root of one *Euphorbia* plant (EU-44) were 143 times greater (14.3 mg kg⁻¹) than the normal levels reported in dry plant tissue (0.1 mg kg⁻¹). Lower Tl concentrations were found in the root and shoot of EU-29 despite higher Tl levels in the EU-29 soil sample. It is interesting to note that the Cu and Zn concentrations (5412 and 18,042 mg kg⁻¹, respectively) in the EU-29 soil sample were 30 and 16 times greater than in those of the EU-44 soil sample (145 and 1585 mg kg⁻¹,

TABLE III
Correlation Relationships Between Tl and Other Metals in Soils of the Keban Mining Area

	Mo	Cu	Pb	Zn	Ag	As
Tl	0.85	0.83	0.85	0.84	0.86	0.85

TABLE II
Thallium and Other Metal Content in Soil With Roots and Shoots of the Studied Samples:
Euphorbia m., Verbascum c., and Astragalus g.

Sample No.	In Plants (in mg kg ⁻¹)														In Soil (in mg kg ⁻¹)						
	Tl	Tl(*)	Mo	Mo	Cu	Cu	Pb	Pb	Zn	Zn	Ag	Ag	As	As	Tl(*)	Mo	Cu	Pb	Zn	Ag	As
EU-21	1.17	1.72(1.56)	85	43	12	3.2	243	13	104	95	0.246	0.173	35	2.6	12.6(11.4)	136	27	654	188	0.66	111
EU-24	0.29	0.47	78	137	15	4.9	152	16	100	100	0.207	0.053	21	2.8	6.7	127	57	687	292	1.15	130
EU-26	0.45	0.49	55	23	30	9	242	14	126	53	0.189	0.039	42	5.2	8.3	313	49	773	449	0.75	380
EU-29	1.46	0.11	686	124	949	33	1985	68	3600	190	3.124	0.124	332	10.2	27.6	2636	5412	7089	18042	24.1	1806
EU-31	0.75	0.46	68	260	15	10	211	32	180	70	0.18	0.113	13	2.9	7.1	423	135	1353	631	1.93	117
EU-34	0.31	0.05	60	68	13	6.3	277	76	269	92	0.247	0.097	20	5.9	4.2	94	35	815	821	0.88	75
EU-41	1.36	0.27	171	39	26	4.8	557	21	186	83	0.308	0.052	39	2.9	10.8	466	61	1600	412	1.46	185
EU-44	4.62	0.05	273	75	44	4.5	1179	49	436	155	1.457	0.142	63	3.7	16.1	578	145	2802	1585	4.48	279
EU-45	0.22	0.05	11	3	19	4.7	338	13	81	15	0.254	0.034	29	1.3	3	22	65	1301	305	1.15	96
VR-25	0.41	0.3(0.28)	81	80	61	27	16	295	194	254	0.104	0.365	3	63.5	11.6(10.5)	115	41	550	593	0.56	423
VR-25Y	0.15	0.23	26	28	40	22	79	140	238	202	0.122	0.215	24	35.8	11.6	115	41	550	593	0.56	423
VR-27	0.68	0.47	9	13	9	10	27	40	26	42	0.055	0.079	24	28.1	4.3	16	3	26	24	0.08	56
VR-35	0.08	0.13	16	16	25	20	138	195	147	237	0.2	0.317	11	22.7	4.2	94	35	815	820	0.88	75
VR-47	0.23	0.18	23	13	18	12	240	218	222	224	0.202	0.291	18	18.6	3	48	33	651	671	0.67	69
AS-22		0.1		95	13			156		102		0.263		18.3	8	114	80	1206	529	2.15	164
AS-28		0.42(0.38)		26	4.7			47		70		0.07		32	14.3(13)	22	5	57	307	0.11	95
AS-32		0.16		402	27			395		208		0.433		25	7	411	127	1365	681	1.88	104
AS-36		0.2		362	30			419		241		0.541		27.1	12.9	1243	240	3640	1190	14.4	129
AS-40		0.58		375	20			552		108		0.308		39.2	12	589	76	1843	407	1.21	142
AS-42		0.67		303	28			528		171		0.394		45.4	13.4	342	96	1713	670	1.5	220

(*): The results in parenthesis represent the values obtained by using ICP-OES.

respectively). Similarly, the Mo and Pb concentrations (2636 and 7089 mg kg⁻¹, respectively) of the EU-29 soil sample were 5 and 3 times greater than those in the EU-44 soil samples (578 and 2802 mg kg⁻¹, respectively).

In addition, Ag and As concentrations of the EU-29 soil samples were greater by 5–6 times than the concentrations of EU-44. As a result, it may be said that these six metals have antagonistic effects on Tl absorption of *Euphorbia* due to their high concentrations (particularly Cu and Zn) in the EU-29 soil sample and their similar chemical properties. The proportion of Tl concentration in shoot to root for EU-29 was found exceedingly lower (0.011) than for EU-44 (0.075). This result proves the antagonistic effect described above, particularly in the Tl uptake from root to shoot. In addition, higher concentrations (Table II) of the metals Mo, Cu, Pb, Zn, Ag, and As in EU-29 in comparison to both EU-44 and other EU-plant parts (especially in root) also prove the antagonistic effects of these metals on Tl uptake by the plant. Distributions of Tl between the studied soil and plant parts are given in Figures 2 and 3. As can be seen, antagonistic effects from the elements can be observed in the plants grown in Cu-, Zn-, Mo-, Pb-, Ag-, and As-rich soils, resulting in lower amounts of Tl taken up by the roots and shoots of the plants.

Tl in *Verbascum*

As can be seen from Table II, the Tl concentrations in both root and shoot of the VR-27 *Verbascum* plant were higher than in the other *Verbascum* samples despite the higher Tl concentrations in the soil samples around these plants. The Mo, Cu, Pb, Zn, Ag, and As concentrations in the soil samples with number VR-25 and VR-25Y were 7–25 times higher than in the soil sample with number VR-27. Thus, it can be said that Mo, Cu, Pb, Zn, Ag,

and As also inhibit the Tl uptake by the VR-25 and VR-25Y *Verbascum* plant from the soil. On the other hand, Tl levels in both root and shoot of the VR-35 *Verbascum* plant and VR-47 *Verbascum* plant were significantly lower than in those of the VR-27 *Verbascum* plant, although the Tl levels of those three soil samples around these three plants were close to each other. These results may also be attributed to the antagonistic effects of Mo, Cu, Pb, Zn, and Ag due to their higher concentrations given in Table II for the VR-35 and VR-47 *Verbascum* soils, which were found higher, that is at least five times than that of VR-27 *Verbascum* soil. Distributions of the Tl concentrations found between the studied soil and plant parts are given in Figures 2 and 4. Antagonistic effects of these elements on Tl uptake and their reflection of Tl content in the root and shoot samples were found to be very similar to the VR-27 *Verbascum* plant.

Tl in *Astragalus*

As can be seen from Table II, the antagonistic effects of Mo, Cu, Pb, Zn, and Ag on the Tl uptake of the *Astragalus* samples (AS-36 and AS-40 *Astragalus* plants) were similar to those described above for the *Euphorbia* and *Verbascum* plants. Although the Tl concentrations in the AS-36 and AS-40 soil samples were very close to each other, the Tl levels in the AS-36 shoots were three times lower than those in the AS-40 shoots. The Mo, Cu, Pb, Zn, and Ag concentrations in the AS-36 soil samples were higher than in the AS-40 soil sample. The Cu, Zn, and Ag concentrations in the AS-36 shoots were also greater than those in the AS-40 shoots. Distributions of the Tl concentrations between the studied soil and the plant parts are given in Figures 2 and 5. These figures show that an increase in Tl concentration in the soil caused the increase in plant Tl concentrations.

From Figure 2 it can be seen that the Tl levels in the all *Euphorbia* roots linearly change with the Tl levels in the soil, except for the EU-44 sample. The corresponding values for VR and AS do not change linearly with Tl in the soil samples. In addition, any clear positive correlation between Tl concentrations in the shoot and the soil samples for the three studied plant species was not observed (Figures 3, 4, and 5). These results can be attributed to the mechanism of Tl uptake by plants from the soil and the Tl transfer to shoots, as well as the other metal levels present in the soil and root samples.

The transfer of toxic metals from soil to plant parts is significantly important because of their subsequent uptake by humans with deleterious consequences. The aim of this study was to determine the relation between Tl concentrations in plant parts and the corresponding soil samples. It can be seen that the transfer of Tl from soil to plant depends on the matrix element concentrations. Scheckel et al. (22) reported higher thallium levels in the leaves of *Iberis intermedia* than in its roots when Tl was added to the soil. In this study, the Tl concentrations of only some shoot samples were found to be higher than in their roots.

CONCLUSION

Most of the observed Tl levels in the *Euphorbia*, *Verbascum*, and *Astragalus* plant samples (including leaves, roots, and surrounding soil) from the Keban mining area of Elazig, Turkey, were found to be higher than the Tl concentrations of uncontaminated soil (higher than 1.0 mg kg⁻¹) and allowable levels for plants (0.05 mg kg⁻¹). It was concluded that such high Tl-containing lands are not suitable agriculture soils because the plants grown in such areas can uptake high and ultimately toxic levels of

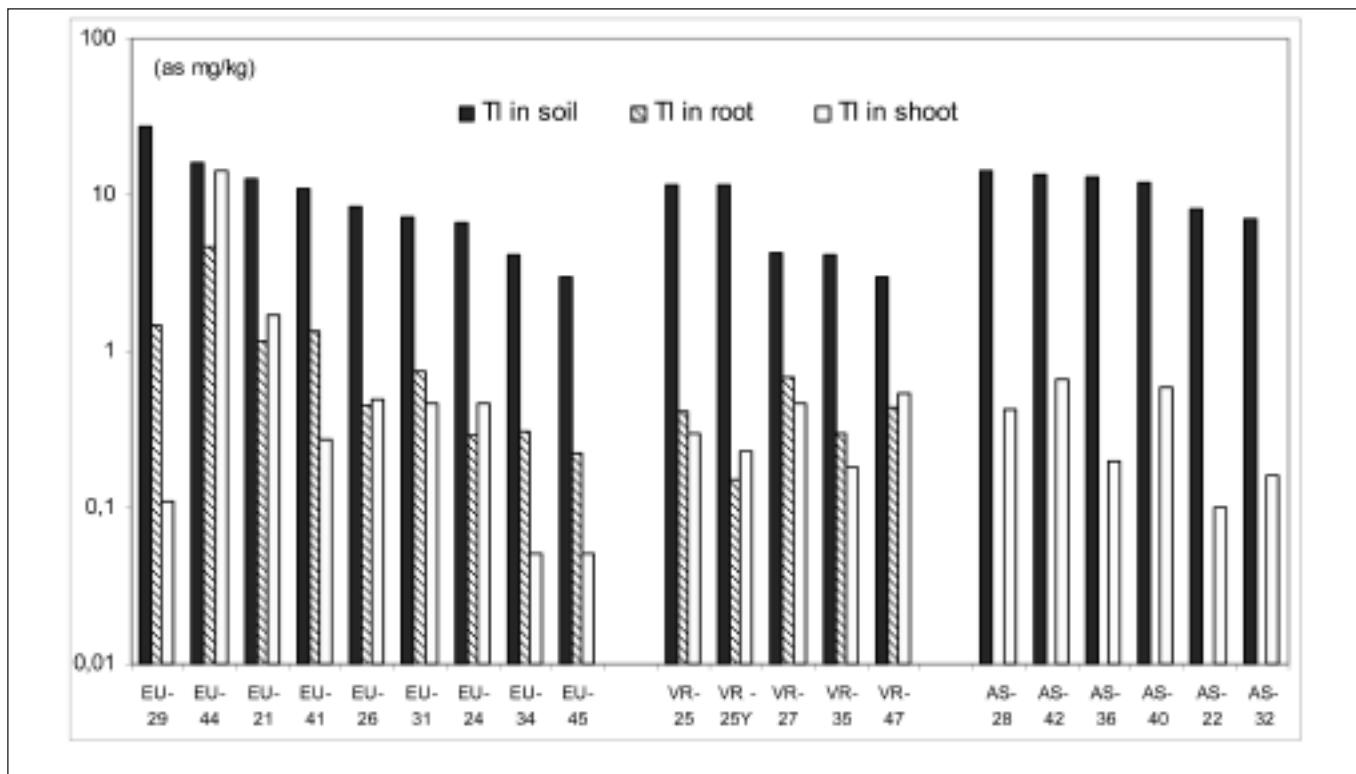


Fig. 2. Histograms for Tl contents of soil, root and shoot samples (EU: Euphorbia, VR: Verbascum, AG: Astragalus) in the Keban mining area.

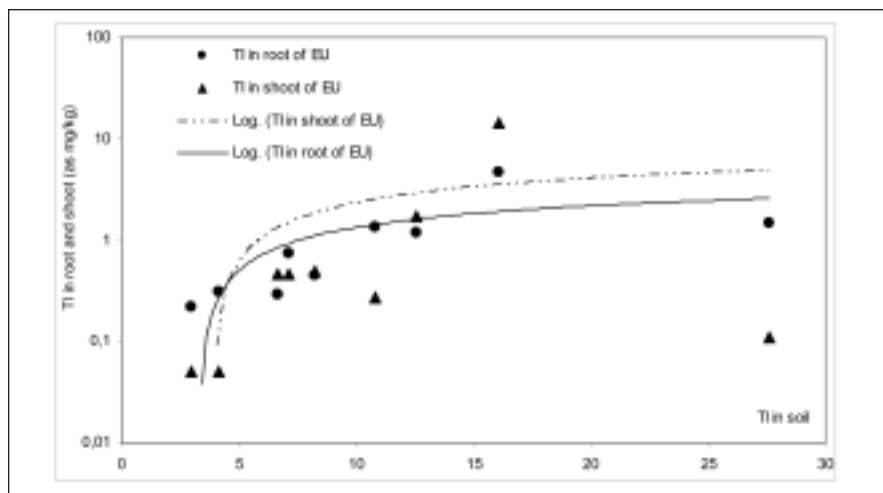


Fig. 3. Correlation relationships for Tl between root and shoot of Euphorbia with soil in Keban mining area.

Tl concentrations. It was also observed that Mo, Cu, Pb, Zn, As, and Ag inhibit the Tl uptake by plant root from soil and by plant shoot from root. It can, therefore, be said that these antagonistic effects can benefit in controlling the Tl uptake abilities of plants.

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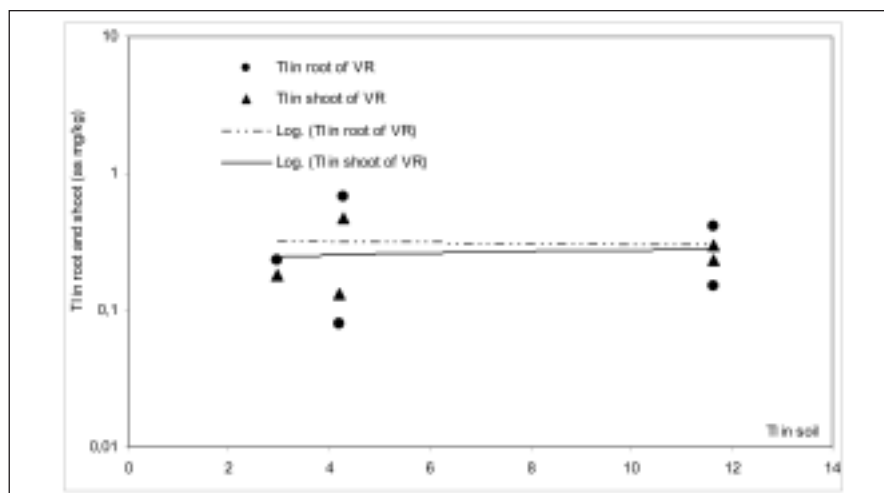


Fig. 4. Correlation relationships for Tl between root-shoot of *Verbascum* with soil in the Keban mining area.

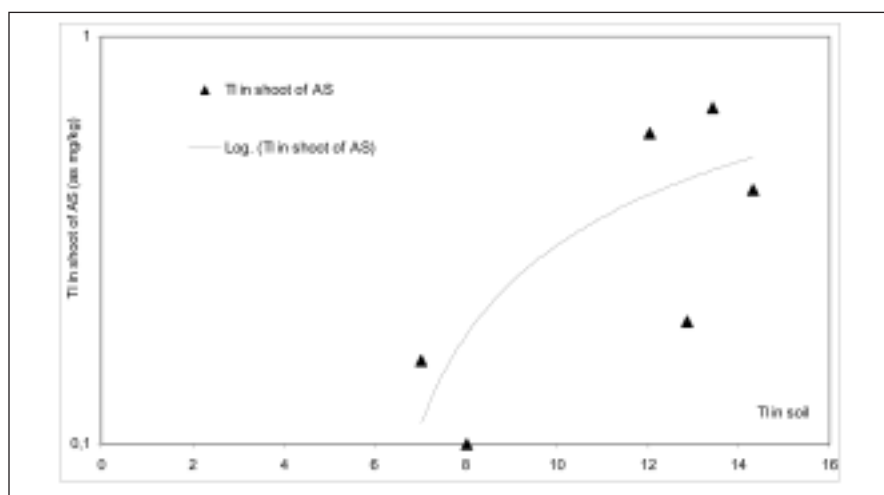


Fig. 5. Correlation relationships for Tl between shoots of *Astragalus* with soil in the Keban mining area.

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A Comparison of ICP-OES and ICP-MS in the Determination of Elements in Lake Water

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INTRODUCTION

Monitoring of trace metals in the environment has been a subject of great concern over the last decade and will continue to be so as there is an ever-increasing quantity of toxic metals found in the environment. The sources of heavy metals in the environment, and more specifically in water systems, have been attributed primarily to anthropogenic sources, such as waste discharge and stack emissions from industrial sources and coal power production. The amounts released vary, with values in millions of tonnes per year for a single metal (1,2). Thus, there exists the need for the continuous monitoring of both fresh water supplies and essentially all water sources, including the oceans, in order to better understand the sources, transport, and amounts of these toxic heavy metals (3). Thus, the need to monitor the elemental composition of a water ecosystem affected by a pollution source is clear (4). The trace element content in water is quite low, often in the $\mu\text{g L}^{-1}$ range, which requires very sensitive analytical methodologies. Previously, trace elements in natural waters were typically determined using flame atomic absorption techniques which, although almost interference-free, are labor-intensive owing to their one-element-at-a-time analytical mode. At the present time, even the furnace atomic absorption technique (for years the standard bearer of low-level trace metal determination) is giving way to other techniques (5). Today, inductively coupled plasma optical emission

ABSTRACT

In this paper, a comparison of two different analytical methods is described based on element composition. The elements Al, Sr, Li, Cu, Pb, Cr, V, and Ni were directly determined in water samples using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The ICP-OES and ICP-MS data were compared and correlation plots were constructed. The correlation between the two methods of analysis varied, with the maximum correlation of 0.999 observed for Pb, and the minimum correlation of 0.907 observed for Sr. The order of the distribution coefficients for the eight metals determined was: $\text{Pb} > \text{Cu} > \text{V} > \text{Ni} > \text{Al} > \text{Cr} > \text{Li} > \text{Sr}$.

spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have become the most popular methods. In this work, a comparison is made of the performance and limitations of these two analytical methods for water pollution studies. Both of these techniques have proven to be reliable and capable for determining a wide range of elements at very low concentration levels simultaneously and accurately (6). In a routine study of lake waters with ICP-OES, some elements are often not detected. It is difficult to say whether they are really absent in the analyzed samples or if they only require a better method of analysis.

However, ICP-MS is a newer technique for trace analysis of liquids (7). Interest in this method has

been increasing over the last 10 years, and the ICP-MS instrument is becoming more common in analytical laboratories. This is the reason that ICP-MS (a more sensitive method) has been used for the determination of elements in water.

For both ICP-OES and ICP-MS, an argon plasma is used as the excitation source, and the detection system is either an optical spectrometer (ICP-OES) or a mass spectrometer (ICP-MS). Although ICP-OES systems are widely available and reasonably cost-effective, the ICP-MS systems have historically required highly trained staff for operation and have been prohibitively expensive. However, their extremely good detection capability, combined with the availability of smaller, more economical spectrometers equipped with good software, is making them increasingly more attractive for the generation of analytical water data (8).

The aim of this paper is to compare the results of the direct determination of important trace elements in real water samples by the two independent analytical techniques (ICP-OES and ICP-MS) and to calculate the correlation coefficients for the measured elements.

EXPERIMENTAL

Instrumentation

A Varian Vista-MPX inductively coupled plasma optical emission spectrometer (ICP-OES) and an Agilent 7500ce ICP-MS with an Octopole Reaction System (ORS) (Agilent, Santa Clara, CA, USA) were used in this work. The ORS consists of an octopole ion guide, mounted off-axis to minimize random

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background levels, inside a cell that can be pressurized with a reaction gas (H_2 and He). Difficult polyatomic interferences such as Ar_2 , $ArCl$, and Ar are dissociated by collision with the reaction gas within the cell, enabling otherwise interfering analytes to be determined (9). Optimization of the chamber was conducted by investigation of the influence of gas used on the received signal of the studied elements. The instrumental and operating parameters for the two instruments are listed in Tables I and II.

Samples

The water samples were collected in acid-cleaned 250-mL Teflon® bottles from 11 locations at Swarzedzkie Lake, Poland. In order to stabilize the dissolved elements, 0.5 mL of Suprapur® nitric acid (Merck & Co., Darmstadt, Germany) was added to each bottle. The samples were stored in a laboratory refrigerator until use. No digestion methods or reduction of the sample volume was done. The samples were analyzed directly.

Standard Solutions, Reagents, and Calibration

Suprapur HNO_3 (65% m/v) was used. Multielemental standard solutions were prepared from 10 mg L^{-1} multielemental atomic absorption standards (Environmental Calibration Standard, Agilent, Santa Clara, CA, USA); calibration standard $n = 1, 2, 3, 4$ by dilution with water containing the same amount of acid as the samples. High purity water was produced from distilled water using a Milli-Q™ deionizing system (Millipore, Bedford, MA, USA). Glassware was cleaned by soaking overnight in a 10% (w/v) nitric acid solution and then rinsing with deionized water.

The elements Al, Sr, Li, Cu, Pb, V, Cr, and Ni were determined according to the International Standard of Water Quality (10,11).

TABLE I
Instrumental Operating Conditions for ICP-OES

Varian Model Vista-MPX CCD Simultaneous ICP-OES	
Plasma argon gas flow rate	15 $L\ min^{-1}$
Auxiliary argon gas flow rate	1.5 $L\ min^{-1}$
Nebulizer argon gas flow rate	0.9 $L\ min^{-1}$
Nebulizer pump	0.10 rps

TABLE II
Instrumental Characteristics and Setting for ICP-MS

Agilent 7500 ce with Octopole Reaction ICP-MS System	
Nebulizer	Micromist
Interface	Ni sampler and skimmer cones
RF generator	1500 W
Argon flows	0.75 $L\ min^{-1}$
Nebulizer pump	0.10 rps
Scanning condition	Number of replicates: 4, dwell time: 1 s
Scanning mode	Pulse
Cell gas flow:	
H_2	3.3 (Cr, V) $mL\ min^{-1}$
He	3.0 (Li, Al, Cr, Cu, Ni, Sr, Pb, V) $mL\ min^{-1}$
Internal standard	^{45}Sc , ^{115}In , ^{133}Cs

Among the aforementioned elements, some occur in higher amounts (called macrocomponents) and others only at trace levels. Not only the elements that are difficult to detect, but also those that give very good analytical results are indicated. Prior to the analysis of the unknown samples, the ICP-OES and ICP-MS methods were validated by analyzing the certified reference materials (CRMs) NIST SRM 1643d Water and NIST SRM 1643e Water (National Institute of Standards and Technology, Gaithersburg, MD, USA). During the course of the study, the control material was run every 10 samples to ensure analytical accuracy. The quality control (QC) data are in given Table III.

RESULTS AND DISCUSSION

Table IV shows the concentrations of eight metals (Al, Cr, Cu, Li, Ni, Pb, Sr, and V) determined by ICP-OES and ICP-MS. Determination of the trace elements Cr, V, and Ni

was not possible with the ICP-OES technique due to the low concentrations present but were able to be determined by ICP-MS. The ICP-OES data obtained for Cu, Pb, and Ni are in good accordance with those obtained by ICP-MS, meaning that ICP-OES is suitable for the determination of these trace elements. The precision values for ICP-MS were significantly better than those for ICP-OES. A comparison of the precision values for the analyzed samples and the CRMs shows that the CRMs were characterized by a much better precision than the natural water samples, especially with ICP-OES, with the exception of Al and Cr for which the RSD was about 18%. RSD values for the CRMs analyzed by the ICP-MS method ranged from 2-5%, except for Al and Cr, for which the RSD values were higher (approximately 2-3%). Precision for the ICP-OES method (only values of precision of the apparatus were

TABLE III
Comparison of Certified Mass Concentration and Determination Value ($\mu\text{g L}^{-1}$)

Element	Certified Value CRM 1643d	Obtained Value ICP-OES	Obtained Value ICP-MS	Certified Value NIST 1643e	Obtained Value ICP-OES	Obtained Value ICP-MS
Al	127.6 \pm 3.5	139.8 \pm 25.0	127.5 \pm 6.9	141.8 \pm 8.6	137.5 \pm 26.9	141.2 \pm 9.82
Cr	18.53 \pm 0.2	16.51 \pm 2.63	18.51 \pm 1.15	20.40 \pm 0.24	18.81 \pm 2.75	20.38 \pm 1.67
Cu	20.5 \pm 3.8	21.58 \pm 2.21	20.53 \pm 1.28	22.76 \pm 0.31	22.53 \pm 2.53	22.73 \pm 0.92
Li	18.53 \pm 0.2	16.91 \pm 2.53	18.51 \pm 1.15	17.4 \pm 1.7	17.52 \pm 2.71	17.36 \pm 1.62
Ni	58.1 \pm 2.7	58.73 \pm 6.41	58.11 \pm 4.12	62.41 \pm 0.69	61.92 \pm 7.92	62.40 \pm 3.21
Pb	18.15 \pm 0.64	17.92 \pm 2.15	18.10 \pm 1.05	19.63 \pm 0.21	19.50 \pm 2.23	19.64 \pm 0.93
Sr	294.8 \pm 3.4	274.3 \pm 34.7	287.1 \pm 13.21	323.1 \pm 3.6	320.6 \pm 27.9	323.7 \pm 5.6
V	35.1 \pm 1.4	35.62 \pm 2.35	34.90 \pm 1.26	37.86 \pm 0.59	37.47 \pm 2.40	37.67 \pm 0.68

Average values \pm standard deviations.

TABLE IV
Concentration of Different Elements (arithmetic mean) in Water Samples
Collected From Different Sites (1 to 11) of Swarzedzkie Lake (P = Precision, R = Reproducibility)

Sampling Stations	Al (mg L ⁻¹)						Sr (mg L ⁻¹)					
	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)
1	0.32	7.4	15.6	0.28	3.3	7.1	0.39	7.0	15.4	0.32	3.1	6.3
2	0.03	6.0	13.3	0.02	2.3	5.0	0.41	8.4	17.1	0.38	2.5	5.3
3	0.06	8.1	16.7	0.03	4.5	8.9	0.38	7.2	15.8	0.34	2.5	5.9
4	0.29	6.2	13.8	0.22	0.2	0.5	0.46	7.5	15.2	0.42	2.3	4.8
5	0.23	5.9	13.0	0.18	0.3	0.6	0.39	6.9	15.4	0.35	2.6	2.9
6	0.42	6.8	14.3	0.35	2.4	5.7	0.46	7.0	15.2	0.44	3.2	6.8
7	0.22	6.3	13.6	0.17	3.0	5.9	0.46	6.5	13.0	0.43	3.3	7.0
8	0.76	6.5	14.7	0.63	3.1	6.4	0.41	8.6	19.5	0.34	2.9	5.9
9	0.48	7.7	14.6	0.42	2.5	4.8	0.42	7.9	16.7	0.45	3.4	6.7
10	0.11	8.9	18.2	0.10	2.3	6.0	0.39	6.8	15.4	0.32	4.0	8.4
11	0.72	5.9	15.3	0.62	2.1	4.8	0.38	9.0	18.4	0.44	4.2	9.1

(continued)

TABLE IV (Continued)
Concentration of Different Elements (arithmetic mean) in Water Samples
Collected From Different Sites (1 to 11) of Swarzedzkie Lake (P = Precision, R = Reproducibility)

Sampling Stations	Cr ($\mu\text{g L}^{-1}$)						Cu ($\mu\text{g L}^{-1}$)					
	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)
1	n.d.	n.d.	n.d.	0.01	4.2	8.9	6.24	5.0	9.9	6.12	2.3	5.4
2	n.d.	n.d.	n.d.	0.029	6.6	13.5	7.25	6.1	12.6	6.78	2.1	5.0
3	1.85	10.3	20.1	0.92	3.5	6.5	5.13	5.7	11.9	4.85	1.5	3.3
4	3.07	8.1	16.9	2.35	2.2	5.1	46.33	6.2	13.0	45.91	1.1	2.5
5	n.d.	n.d.	n.d.	0.046	2.1	4.4	2.13	5.0	10.8	1.85	1.8	3.8
6	1.64	10.9	20.6	1.13	2.6	5.3	14.46	4.8	10.1	14.83	2.3	4.9
7	0.12	8.0	16.7	0.088	2.2	4.6	5.43	6.0	13.1	5.54	2.4	5.1
8	10.07	7.4	15.2	8.32	2.8	5.5	460.16	5.6	11.7	465.20	2.2	4.6
9	n.d.	n.d.	n.d.	0.025	1.8	4.0	10.53	6.7	13.1	10.73	2.5	4.9
10	0.86	7.8	18.6	0.57	2.6	5.3	4.62	6.1	12.8	4.67	2.5	5.6
11	0.16	6.1	12.5	0.11	2.0	4.6	6.23	5.5	11.7	6.08	2.7	5.3

n.d.: not detected.

(continued)

TABLE IV (Continued)
Concentration of Different Elements (arithmetic mean) in Water Samples
Collected From Different Sites (1 to 11) of Swarzedzkie Lake (P = Precision, R = Reproducibility)

Sampling Stations	Li ($\mu\text{g L}^{-1}$)						Ni ($\mu\text{g L}^{-1}$)					
	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)
1	6.19	7.5	16.0	5.81	2.4	4.8	0.076	9.0	18.4	0.048	2.1	4.2
2	6.21	10.0	19.8	5.78	4.1	8.3	0.18	8.1	16.7	0.08	3.0	6.3
3	6.14	10.7	20.8	5.63	2.0	4.3	0.82	8.8	18.3	1.07	3.2	6.5
4	7.06	10.2	19.0	5.78	3.2	6.6	1.62	8.5	17.9	2.14	2.4	5.1
5	7.03	8.9	18.4	6.17	4.0	7.6	0.27	8.9	18.5	0.48	2.9	6.3
6	7.12	9.3	19.0	6.68	3.0	6.0	0.14	9.9	19.6	0.33	2.7	6.1
7	7.15	8.6	17.6	7.12	2.7	5.9	0.20	10.0	20.0	0.42	3.6	7.1
8	7.21	7.0	15.5	7.18	3.7	7.4	4.90	8.7	18.0	6.20	2.2	5.0
9	7.02	10.1	19.8	6.63	2.5	5.6	8.07	8.9	18.1	10.49	3.2	6.6
10	7.21	12.3	20.4	7.17	2.8	5.3	1.05	9.2	18.1	2.22	2.6	5.0
11	7.11	7.2	13.8	6.78	3.1	6.3	0.055	7.6	16.4	0.21	2.1	4.8

(continued)

TABLE IV (Continued)
Concentration of Different Elements (arithmetic mean) in Water Samples
Collected From Different Sites (1 to 11) of Swarzedzkie Lake (P = Precision, R = Reproducibility)

Sampling Stations	Pb ($\mu\text{g L}^{-1}$)						V ($\mu\text{g L}^{-1}$)					
	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)	ICP-OES	P (%)	R (%)	ICP-MS	P (%)	R (%)
1	3.32	7.8	16.0	3.26	2.3	4.9	n.d.	n.d.	n.d.	0.086	2.3	4.7
2	n.d.	n.d.	n.d.	0.026	4.9	8.9	n.d.	n.d.	n.d.	0.074	2.0	4.1
3	1.45	9.2	18.6	1.12	2.6	5.4	0.12	8.2	16.8	0.093	3.0	5.4
4	16.21	7.1	15.00	16.54	2.5	5.2	n.d.	n.d.	n.d.	0.051	1.7	3.9
5	16.65	7.5	15.7	16.91	3.0	5.7	0.13	7.4	15.4	0.072	2.0	4.2
6	9.46	6.0	13.3	9.32	1.8	3.9	0.42	7.0	14.3	0.24	2.1	4.2
7	5.52	5.8	12.0	5.42	2.2	4.6	0.54	7.3	14.8	0.43	2.6	4.7
8	32.21	7.9	16.2	33.21	2.4	5.1	2.11	8.3	17.5	2.18	2.2	5.0
9	12.73	6.3	13.0	12.68	2.0	4.4	1.15	6.9	14.8	1.31	3.0	6.1
10	2.23	8.5	17.0	2.26	2.7	5.3	n.d.	n.d.	n.d.	0.048	1.7	4.2
11	n.d.	n.d.	n.d.	0.028	3.4	7.1	n.d.	n.d.	n.d.	0.013	3.7	7.7

n.d.: not detected.

taken into consideration) was between 4.8–12.3%, but reproducibility was between 10.1–20.6%. Reproducibility and precision for the ICP-MS method were significantly lower and ranged from 0.2–6.9% and 0.5–13.5%, respectively. Comparing the obtained values of reproducibility for the ICP-MS method with those established by the ISO standards (11) ranging from 6.9–27%, we can see that the ICP-MS values obtained in our laboratory are considerably lower.

Figure 1 (a–h) represents correlation plots for the elements Al, Cr, Cu, Li, Ni, Pb, V, and Sr determined by using both the ICP-OES and ICP-MS techniques. The dotted lines in this figure represent a $\pm 5\%$ error bar.

Results of the various analytical techniques using correlation analysis with the linear regression (LR) method were collated based on the equation: $y = a + bx \pm \text{error}$. For comparison, R (Regression coefficient), slope (b) and intercept (a)

were evaluated, which in a theoretical model assume the following values: $R = 1$, $b = 1$, and $a = 0$. If the two variables were equivalent, the real and the ideal regression line should be equal or similar. The best values of statistical parameters were observed by comparing the two methods for Cu and Pb (0.997 and 0.999, respectively). Satisfactory values were observed for Ni (0.989), V (0.989), Al (0.988), and Cr (0.988), although as mentioned before, the determination of ^{52}Cr by ICP-MS suffers a spectral interference; therefore, the measurements made using that technique gave less accurate results than those obtained by ICP-OES (12). The comparison for Li and Sr yielded values that were not so satisfactory. The correlation coefficients for these elements were 0.923 and 0.907. It is clear that the error bars in the x direction are significantly higher than those in the y direction. The values obtained using ICP-OES, lower than those obtained by ICP-MS, reveal the greatest difference between the techniques in the mea-

sured levels. The limits of detection (LODs) were calculated as a sum of average values for 10 independently prepared blank solutions and three standard deviations of the measurements of the blank solution ($\text{LOD} = \bar{X} + 3\sigma$) (13). The ICP-MS method showed lower detection limits, many times lower than those obtained with ICP-OES. Thus, it can be stated that the results obtained with these two analytical methods were in general similar or equal, but not completely interchangeable.

CONCLUSION

The results presented in this work demonstrate the possibilities offered by the two analytical methods (ICP-OES and ICP-MS) used in the performed research. The obtained results show low concentrations of the elements in the collected water samples. The ICP-OES and ICP-MS data were compared, and the correlation plots show excellent agreement between the values obtained for Cu and Pb;

Fig. 1 (a - b). Correlation plots of Al, Cr, Cu, Li, Pb, Sr and V concentrations in the water samples analyzed by ICP-OES (x) versus ICP-MS (y).

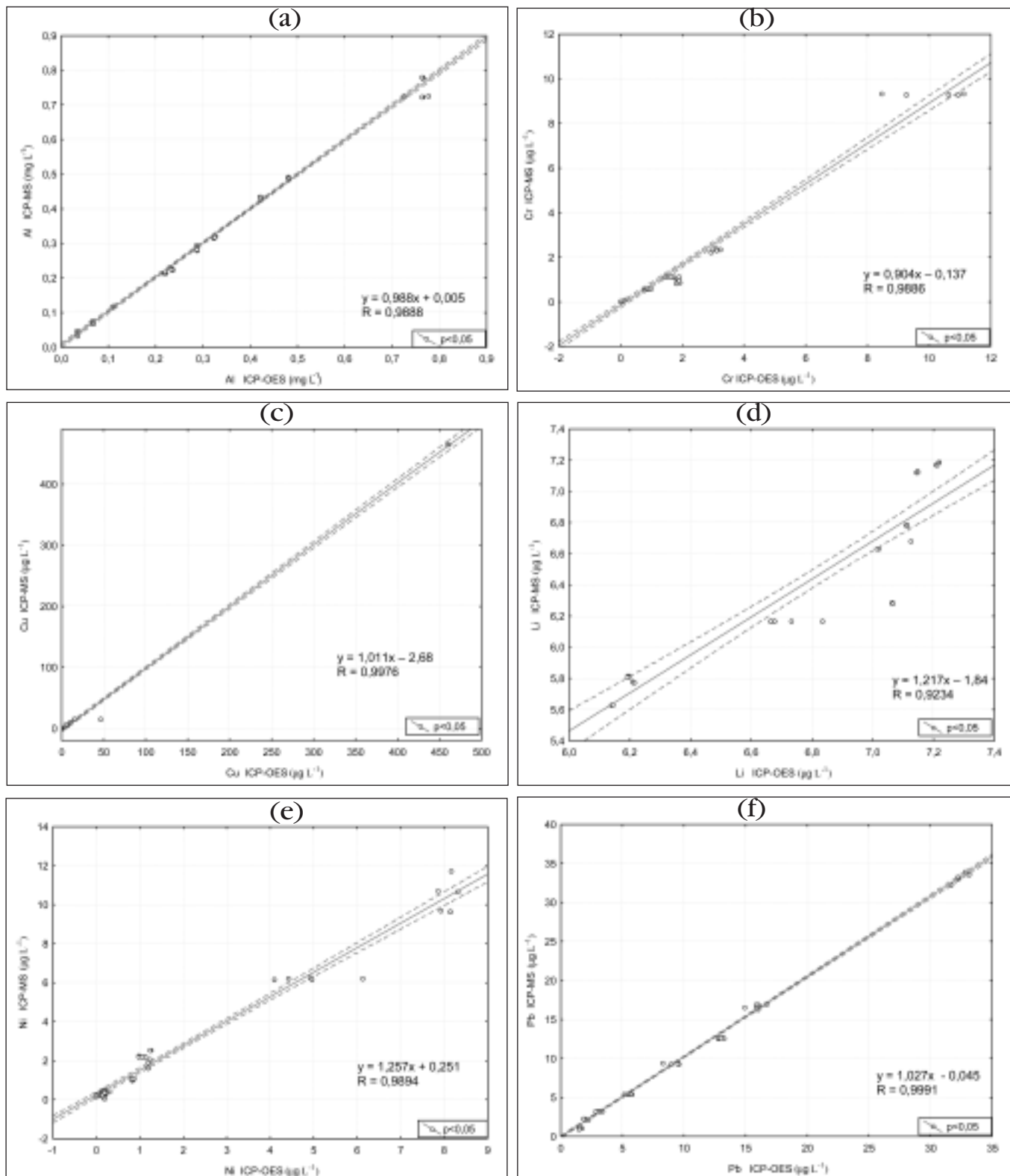
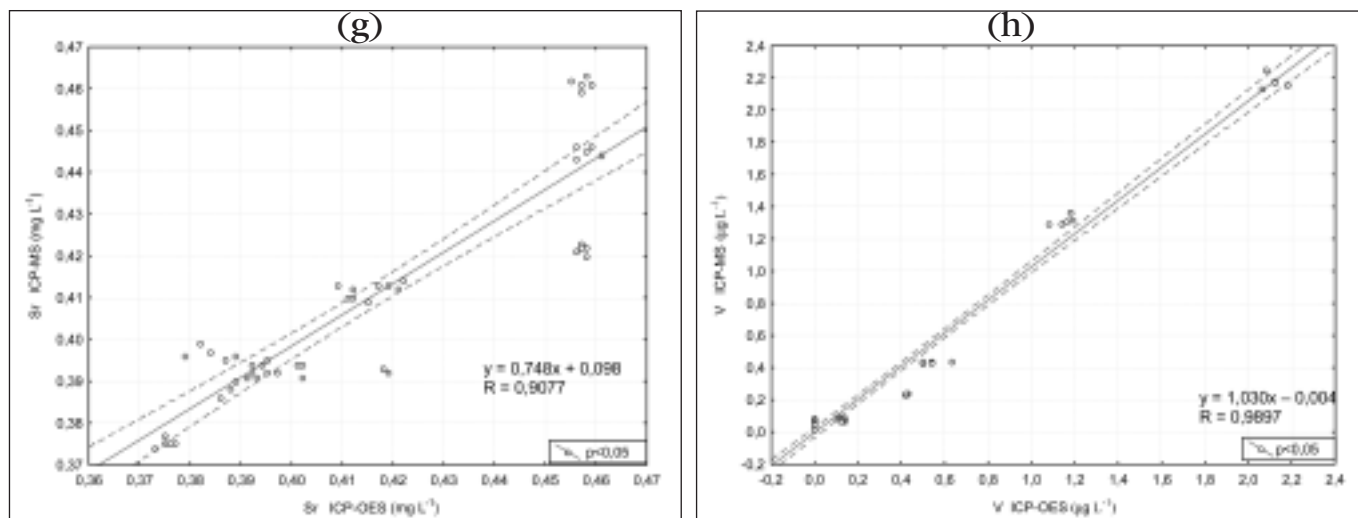


Fig. 1 (a – b). Correlation plots of Al, Cr, Cu, Li, Ni, Pb, Sr and V concentrations in the water samples analyzed by ICP-OES (x) versus ICP-MS (y).



good agreement obtained for Al, Cr, V, and Ni; however, they highlight the fact that ICP-MS provides better precision than ICP-OES. Precision for the ICP-OES method was between 4.8–12.3%, but precision for the ICP-MS method was significantly lower and ranged from 0.2–6.9%. The poor values of the correlation coefficients obtained for Li and Sr by ICP-OES may be attributed to the lower limit of detection for these two elements.

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Preconcentration and Speciation of Sb(III) and Sb(V) With Alumina Mini Column and Determination by Flame AAS

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INTRODUCTION

There is an ever-increasing demand in environmental research for analytical methods that can determine toxic elements at trace levels. Antimony is an element of environmental concern due to its toxicity and biological effects. It is a nonessential element and its toxicity is comparable to that of arsenic (1). Analytical methods must be developed to monitor different chemical forms of antimony in the environment, because its toxicity and biological effects greatly depend on the oxidation state of this element and inorganic species of antimony are more toxic than their organic counterparts (2).

One problem in inorganic Sb speciation is the low concentration of these species in natural samples. For example, the maximum admissible concentration of Sb in drinking water is 10 $\mu\text{g L}^{-1}$ (3).

Antimony is released into the environment and enters the aquatic system, especially as a result of rock weathering, soil runoff, mining activities, road traffic and municipal discharges (4).

However, speciation of Sb compounds is attracting increasing attention from the scientific community and, as a result, the number of published analytical procedures dealing with antimony speciation is increasing. Techniques such as atomic absorption spectrometry (AAS) (5), inductively coupled plasma atomic emission spectrometry (ICP-AES) (6), ion chromatogra-

ABSTRACT

A method of antimony speciation is described based on the retention and selective elution of Sb(III) and Sb(V) from a mini column packed with acidic alumina using KOH and HCl solution as the eluents. Before passing the samples through the mini column, alumina was treated with phosphoric acid. Phosphoric acid was immobilized on the alumina and retained both antimony species. Sb(V) was selectively eluted by the KOH solution and then Sb(III) was washed out using an HCl solution.

The pH and volume of the sample solutions, the volume and concentration of the phosphoric acid and eluent solutions were optimized.

Interference studies were carried out and the suitability of the proposed method for the preconcentration and speciation of antimony in real samples was evaluated. The detection limits (3 σ) were 0.3 and 1.1 ng mL^{-1} (25- and 50-fold preconcentration factor) and the linearity range was 5–100 and 9–10 ng mL^{-1} for Sb(V) and Sb(III), respectively.

The RSD for five replicate measurements of 100 ng mL^{-1} of Sb(V) was 2% and for Sb(III) it was 2.4%. Spike recoveries were tested at various concentration levels for different water samples and were found to vary between 96 and 104%.

phy (7), and ICP mass spectrometry (ICP-MS) (8) have been used for antimony speciation. However, these techniques are either not sufficiently selective or not easily adaptable to routine analysis (1). Atomic absorption spectrometry

with hydride generation (HG-AAS) is the most widely used technique (9). In this technique, the selective determination of Sb(III) is carried out in the presence of Sb(V) and then total antimony is determined. The concentration of Sb(V) can be obtained by calculating the difference. An alternative method of antimony speciation also using HG-AAS requires a somewhat lengthy process of extraction and separation of both species (10).

The most recent publication dealing with this matter is a paper describing simultaneous determination of Sb(III) and Sb(V) by UV-Visible spectroscopy and the partial least squares method (2). This method is adaptable to routine analysis but is not sensitive. The minimum concentration determinable by this method for these two antimony species is reported to be about 4.8 mg L^{-1} (2). Smichowski et al. reported speciation and preconcentration of Sb(III) and Sb(V) on phosphoric acid-treated alumina under pH-controlled conditions (11). At pH 9.5, the retention of Sb(V) on the alumina is negligible (less than 1%) while Sb(III) is selectively eluted and can be quantitatively determined. At pH 7.5, both species are retained and total antimony is determined. The Sb(V) is obtained by calculating the difference.

The present paper describes a method for the preconcentration and separation of Sb(V) and Sb(III) using a phosphoric acid-treated alumina mini column. Sb(V) and Sb(III) are selectively eluted by KOH and HCl solutions, respectively, before their determination by flame

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atomic absorption spectrometry (FAAS).

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Instrumentation

For this study, a PerkinElmer® Model 1100B atomic absorption spectrometer equipped with a deuterium background corrector and an air/acetylene flame with a flow rate ratio of 8/2.5 mL min⁻¹ and 2200 °C temperature was used throughout the work (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The monochromator was adjusted to the 217.6 nm wavelength and a slit width of 0.2 nm.

All solutions were transferred into the column by a Master flex single-channel standard peristaltic pump with a current volume range of 0.6 to 228 mL min⁻¹ and a maximum external pressure of 25 PSI.

A six - port low pressure manually operated injection Rheodyne® valve Model 7010, fitted with a 2-mL loop, was used to introduce sample, eluent and carrier into the minicolumn fabricated from stainless steel with an internal diameter of 1.8 mm and a length of 7 cm.

The column was packed with 0.3 g acidic alumina (obtained from Fluka, Buchs, Switzerland, of pH = 4.5 ± 0.3).

Reagents and Solutions

Doubly distilled and deionized water (obtained from SG Treatment & Regeneration System, Barsbüttel, Germany) was used throughout. 3M phosphoric acid was used for alumina conditioning; 1M potassium hydroxide and 8M hydrochloric acid solutions were used as the eluents.

Stock standard solutions (100 µg mL⁻¹) of Sb(III) and Sb(V) were prepared by dissolving appropriate amounts of potassium antimony tartarate and potassium pyroantimonate (obtained from

Fluka, Buchs, Switzerland) in distilled water respectively and diluting to 100 mL.

The stock solutions were stored in polyethylene bottles at 4 °C. All working standard solutions of Sb(III) and Sb(V) were prepared daily prior to use to prevent any possible species change.

All reagents used were of analytical grade and obtained from Fluka.

Procedure

The analytical system, which includes the injection valve modes, mini column, peristaltic pump, and atomic absorption spectrometer, is presented in Figure 1.

Slightly more than 2 mL of the sample was injected into the 2-mL loop when the valve was operating in the LOAD mode (Figure 1b) and, simultaneously, the carrier solution (distilled water) was pumped through the mini column at a flow rate of 4 mL min⁻¹ via ports 2 and 3. Then the sample was passed through the alumina column by operating the valve in INJECT mode (Figure 1b).

The retained Sb(V) was then eluted from the alumina by passing 4 mL of 1M KOH solution through the mini column. Before elution of the retained Sb(III), the alumina sorbent was washed out of the KOH residue by pumping 2 mL of

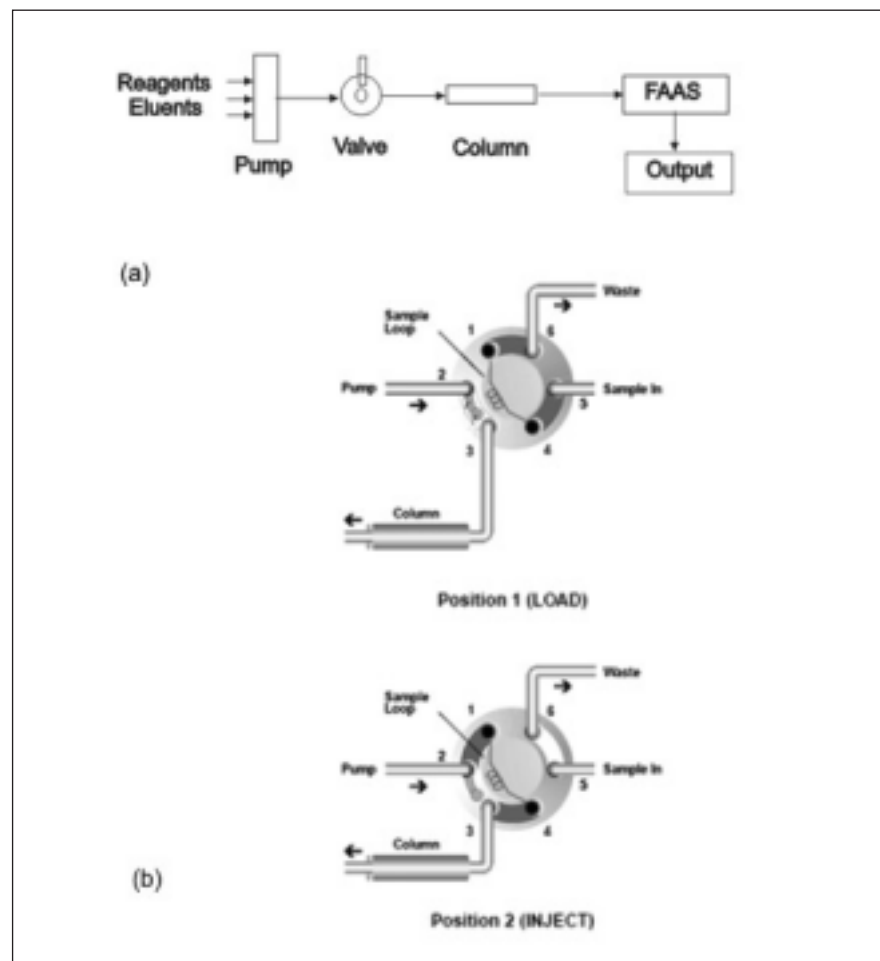


Fig. 1. (a) Layout of the analytical system and (b) injection valve operation modes used for antimony preconcentration and speciation.

1M perchloric acid into the column. Finally, the Sb(III) was eluted with 2 mL of 8M HCl solution. Potassium hydroxide and perchloric and hydrochloric acids were pumped through the mini column via ports 2 and 3 of the valve operating in LOAD mode and at the flow rate of 4 mL min⁻¹.

Prior to the sample injection, the alumina sorbent was conditioned by passing 10 mL of 1M phosphoric acid solution through the mini column and then washing with 10 mL distilled water. This acid solution was also pumped through the alumina column at the flow rate of 4 mL min⁻¹ and via ports 2 and 3 of the valve operating in LOAD mode. The column must be conditioned after speciation of 100 samples.

The operating procedure was carried out in the following steps:

- Injection of 2 mL of the sample into the mini column.
- Elution of the retained Sb(V) from alumina with 4 mL of 1M KOH solution.
- Collection of the eluate and determination of Sb(V) with FAAS.
- Washing the column with 2 mL of 1M perchloric acid.
- Elution of the retained Sb(III) from alumina with 2 mL of 8M hydrochloric acid.
- Collection of the eluate and determination of Sb(III) by FAAS.

Preconcentration of the antimony species was carried out by pumping 100 mL of the sample through the alumina and eluting the retained Sb(V) and Sb(III) with 4 mL KOH and 2 mL HCl solution, respectively.

RESULTS AND DISCUSSION

McLeod (12) has demonstrated that the acidic form of activated alumina has a high affinity for oxoanion species. It is also known

that antimony has a high capacity for forming a variety of complexes with phosphoric acid (11,13). The differences in the behavior of Sb(III) and Sb(V) in phosphoric acid can be explained by the different stability of the complexes formed between the antimony species and this acid (11).

Based on these reported results, a method was developed for the preconcentration and speciation of Sb(III) and Sb(V). Phosphate oxoanion was adsorbed on the alumina by treating this sorbent with phosphoric acid.

Two complexes with different stability were formed between this immobilized phosphate anion and Sb(III) and Sb(V) on passing these species in distilled water media through the alumina mini column. Two specific eluents were used to elute selectively and separate these two complexes.

Variables Affecting Method Optimization

In order to determine the optimum conditions, the effect of some chemical and physical parameters on the Sb(III) and Sb(V) signals were investigated. The peak height of the absorbance signals were compared with those of solutions of Sb(III) and Sb(V) that had not passed through the alumina column. The recovery was calculated as the ratio of the two absorbance values for each antimony species.

Eluent Selection

The possibility of Sb(III) and Sb(V) separation by using alumina sorbent and suitable eluents was evaluated. To evaluate this possibility, solutions of KOH and four acids (HCl, HNO₃, HClO₄, and H₂SO₄) were tested as the eluent. By using each eluent, the recovery of each antimony species was determined.

Two mL of each Sb(III) and Sb(V) standard solution (2.5 mg L⁻¹) was injected into the sorbent and then eluted by the appropriate eluent. The collected eluate was analyzed and the recovery was calculated.

By using 2 mL of 1M HCl eluent, 91% of Sb(III) and 55% of Sb(V) were recovered together. By passing a more concentrated HCl (3M), an enhancement in the recoveries was observed [99% and 60% for Sb(V) and Sb(III), respectively]. Employing 4 mL of 0.5M KOH as the eluent showed that only Sb(V) can be recovered (92%) and Sb(III) is retained completely (0.0% recovery). By introducing 4 mL of 1M KOH and then 2 mL of 3M HCl through the mini column (which was already loaded with a binary standard solution of both antimony species), Sb(V) and Sb(III) were selectively eluted with recoveries of 100% and 60%, respectively.

To investigate the possible enhancement of Sb(III) recovery, four other acids (HNO₃, H₂SO₄, HClO₄ and CH₃COOH) were also tested as eluents. In each test, 2 mL of Sb(III) standard solution was injected into the column which was then eluted by a 3M solution of each acid and the recoveries were determined by FAAS. Before elution with each acid, 4 mL of 1M KOH was passed through the column. The results of these experiments are shown in Table I. However, HCl and KOH were selected as convenient eluents.

TABLE I
Sb(III) Recoveries
Using Different Acid Eluents

Acids ^a	Recovery (%)
HNO ₃	8.0
HAc	4.0
HClO ₄	0.0
H ₂ SO ₄	11.0

^a 3M solutions.

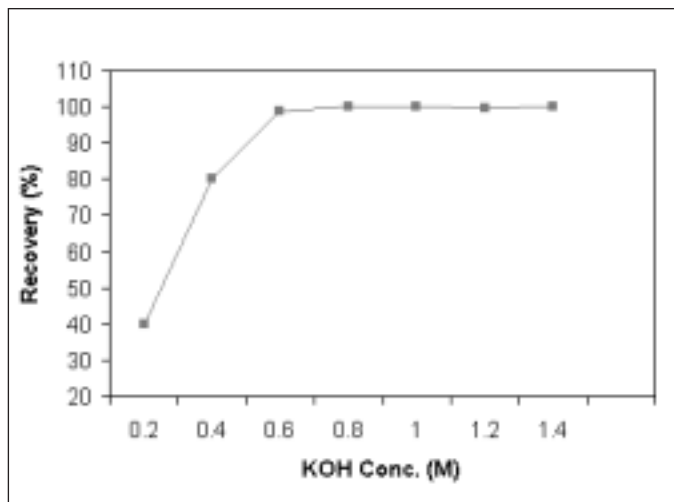


Fig. 2. Effect of KOH concentration on the recovery of Sb(V). Conditions: Sb(III) and Sb(V) concentrations 2.5 mg L^{-1} ; volume of samples 2 mL; 10 mL of 3M H_3PO_4 ; eluents: 2 mL of 8M HCl and 4 mL of KOH; sample pH = 7; 1 mL of 1M HClO_4 .

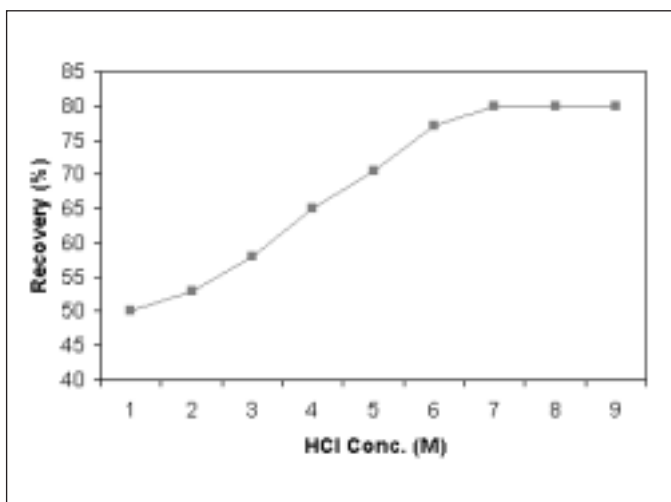


Fig. 3. Effect of HCl concentration on recovery of Sb(III). Conditions: eluents: 2 mL of HCl and 4 mL of 1M KOH. The rest of the conditions were the same as indicated in Figure 2.

It was also found that the recovery of Sb(III) increases if the column is washed out from the KOH residue with 2 mL of 1M perchloric acid prior to the elution of Sb(III) with HCl and after the elution of Sb(V) with KOH. The retention of the Sb(III) is not affected by perchloric acid (see Table I).

The effect of these eluent concentrations on the recovery of the antimony species was also studied. The results given in Figures 2 and 3 show that the recoveries of Sb(V) and Sb(III) increases as KOH and HCl concentrations are increased up to 1M and 8M, respectively. Therefore, these concentrations were adopted as the optimum concentrations.

Effect of Phosphoric Acid Concentration

Phosphoric acid with different concentrations and used as the alumina activating agent was examined. The volume of acid passing through the column was 10 mL at all concentrations and the operating procedure described above was followed. Each test was carried out

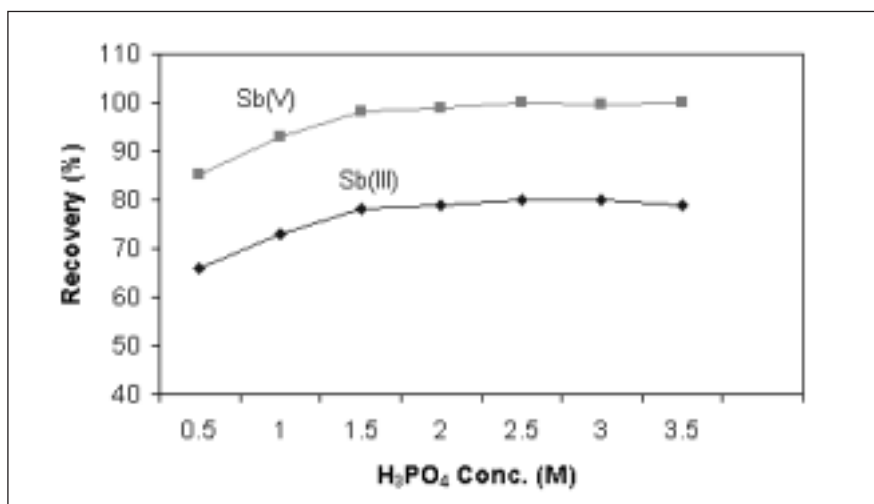


Fig. 4. Influence of phosphoric acid concentration on the recovery of Sb(III) and Sb(V). Conditions: Sb(III) and Sb(V) concentrations 2.5 mg L^{-1} ; volume of samples 2 mL; 10 mL H_3PO_4 ; eluents: 2 mL of 8M HCl and 4 mL of 1M KOH; sample pH = 7; 2 mL of 1M HClO_4 .

with a new repacked column. The results in Figure 4 show that by increasing the phosphoric acid concentration up to 1.5M, the recoveries of Sb(III) and Sb(V) were increased, after which they remained constant. Since the number of samples that can be loaded

into the column before its exhaustion depends on the phosphoric acid concentration, a 3M concentration was selected as the optimum value.

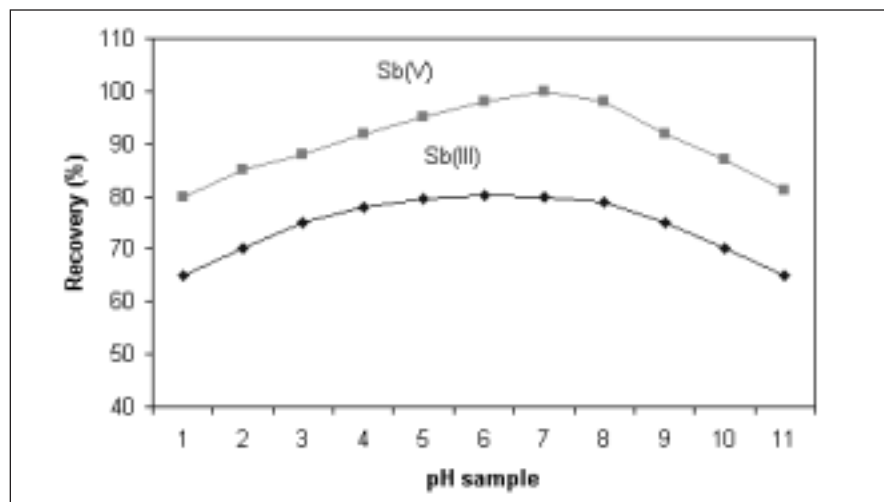


Fig. 5. Effect of sample pH on the recovery of Sb(III) and Sb(V). Conditions: Sb(III) and Sb(V) concentrations 2.5 mg L^{-1} ; volume of each sample 2 mL ; 10 mL of $3 \text{ M H}_3\text{PO}_4$; eluents: 2 mL of 8 M HCl and 4 mL of 1 M KOH ; 2 mL of 1 M HClO_4 .

Effect of Sample pH

Since the pH of the sample solution is an important parameter affecting the recoveries of antimony ions (11), the retention of Sb(III) and Sb(V) was studied as a function of sample pH. For this purpose, the pH values of two standard solutions (2.5 mg L^{-1}) of Sb(III) and Sb(V) were adjusted from pH 3–11 with appropriate acid and base solutions. The recovery of the antimony species was then determined by following the operating procedure. The results given in Figure 5 show that the maximum recovery of Sb(III) and Sb(V) were obtained at around pH = 7.

Interference Studies

Using optimized conditions, the effect of diverse ions on antimony speciation was studied. The interfering effects of anions such as vanadate, dichromate, arsenate, arsenite, selenate, sulphate, nitrate, nitrite, acetate, phosphate, fluoride, chloride, bromide, and iodide, along with cations such as ammonium, potassium, sodium, magnesium, and chromium, were studied. In this study, synthetic solutions containing 2.5 mg L^{-1} of each anti-

mony species and various amounts of foreign ions were prepared and the operating procedure was followed. The tolerance ratio was defined as the maximum concentration ratio of foreign ions to Sb(III) or Sb(V) giving an error of less than 5%. As can be seen from Table II, almost none of the ions interfere in the antimony speciation at concentration ratios greater than 100, with the exception of fluoride.

The only interfering ion (fluoride) showed its interfering effect at the 10/1 ratio (F^{-1}/Sb). Further studies indicated that at a concentration ratio of 8/1, the fluoride ion inter-

ference causes an error of less than 5%. Investigation of the fluoride interference effect showed that at fluoride presence (at a ratio of 10 or higher), Sb(V) is not retained quantitatively by alumina.

Preconcentration

The very low concentration of Sb in most natural samples makes it necessary to examine the applicability of the proposed method for preconcentration of the antimony species.

A binary solution containing $50 \text{ } \mu\text{g L}^{-1}$ of each antimony species was used for this study. Different volumes of this solution from 50 to 200 mL were pumped through the column at a flow rate of 4 mL min^{-1} via ports 2 and 3 of the valve (Figure 1b) operating in LOAD mode.

By using sample volumes up to 100 mL, no drop in recoveries of Sb(III) and Sb(V) was observed. Increasing the sample volume to 150 mL caused a 5% drop in Sb(III) retention, but there was no effect on the Sb(V) recovery. The Sb(V) recovery was quantitative even when up to 250 mL of the sample was employed.

The antimony retention kinetics was studied in the $1\text{--}6 \text{ mL min}^{-1}$ range by preconcentrating 100 mL of $50 \text{ } \mu\text{g mL}^{-1}$ of Sb(III) and Sb(V). Analysis of the solution collected after passing through the mini col-

TABLE II
The Effect of Foreign Ions on the Determination of 2.5 mg L^{-1} Sb(III) or Sb(V)

Interferent	Tolerance ^a
K^+ , NH_4^+ , Na^+ , Mg^{2+} , Ni^{2+} , SO_4^{2-} , NO_2^- , NO_3^- , CH_3COO^- , PO_4^{3-}	1000
Br^- , I^- , Cl^-	500
Cr(III) , Cr(V) , As(III) , Se(IV) , V(VI)	200
F^-	8

^a Maximum concentration ratio of interfering species to Sb(III) or Sb(V) giving an error of <5%.

umn revealed no detectable anti-mony species for either case. Therefore, it was concluded that the flow rate of the sample solution was not a critical factor.

The flow rate of 4 mL min⁻¹ was chosen as the optimum for preconcentration.

However, the preconcentration factor for Sb(V) and Sb(III) was evaluated to be 25 and 50, respectively.

Analytical Performance and Applications

The proposed method was applied to the preconcentration of Sb(V) and Sb(III) in the ranges of 5–100 µg L⁻¹ and 9–100 µg L⁻¹, respectively. The calibration graph was linear for Sb(V) with an equation of:

$$A_1 = 5.4 \times 10^{-3} C_1 - 0.017 \times 10^{-3}$$

where C_1 is the concentration of Sb(V) in µg L⁻¹ of the initial solution (100 mL), with $r = 0.9994$. For Sb(III), the calibration graph was linear with an equation of:

$$A_2 = 3.2 \times 10^{-3} C_2 - 4.2 \times 10^{-3}$$

where C_2 is the concentration of Sb(III) in µg L⁻¹ of the initial solution, with $r = 0.9973$. The concentration ranges in the final solution were 0.125–2.5 mg L⁻¹ for Sb(V) and 0.450–5 mg L⁻¹ for Sb(III).

The analytical performance of the proposed procedure is shown in Table III.

The applicability of the proposed method for speciation of antimony was carried out by measuring the Sb(V) and Sb(III) concentrations in four different spiked samples. Spiked sample solutions (100 mL) of tap, underground, sea, and river water were subjected to the operating procedure. As shown in Table IV, good recoveries were obtained.

TABLE III
Analytical Performance

	Sb(V)	Sb(III)
Linear Range	5 – 100 µg L ⁻¹	9 – 100 µg L ⁻¹
Sensitivity	5.4 x 10 ⁻³ a.u. (µg L ⁻¹) (f = 25) ^a	5.4 x 10 ⁻³ a.u. (µg L ⁻¹) (f = 50)
Detection Limit (3σ) ^b	0.3 µg L ⁻¹ (f = 25)	1.5 µg L ⁻¹ (f = 50)
Precision ^b	2% (for 100 µg L ⁻¹)	2.4% (for 100 µg L ⁻¹)

^a f = Preconcentration factor.

^b (n = 6).

TABLE IV
Spiked Water Sample Analysis and Recovery Studies

Sample	Sb Added (µg L ⁻¹)		Sb Found ^a (µg L ⁻¹)		Recovery (%)	
	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)
Tap Water	0.00	0.00	–	–	–	–
	10.00	10.00	9.8 ± 0.3	9.6 ± 0.3	98.0	96.0
	80.00	80.00	79.5 ± 1.5	80.1 ± 2.05	99.4	100.1
Underground Water (South of Tehran)	0.00	0.00	–	–	–	–
	10.000	10.00	14.2 ± 0.18	10.2 ± 0.22	142.0	102.0
	70.00	70.00	73.4 ± 1.1	69.8 ± 0.20	104.8	99.7
Caspian Seawater	0.00	0.00	–	–	–	–
	20.00	20.00	20.4 ± 0.49	20.2 ± 0.55	102.0	101.0
	55.00	55.000	56.1 ± 1.00	55.8 ± 1.20	102.0	101.8
Jajrood River Water (East of Tehran, Industrial Zone)	0.00	0.00	–	–	–	–
	35.00	35.00	34.50 ± 0.73	35.00 ± 0.80	98.7	100.0
	70.00	70.00	71.00 ± 1.20	69.4 ± 0.75	101.4	99.1

^a Based on five measurements.

CONCLUSION

The proposed method allows the separation, determination, and simultaneous preconcentration of inorganic species of antimony [Sb(III) and Sb(V)] in a single sample. The majority of reported methods determine total antimony and one of the Sb species and then cal-

culate the concentration of the other species by the difference. However with the presented method, the concentration of both antimony species was measured.

The method is simple, sensitive, sufficiently and easily adaptable to routine and on-line analysis.

The method was successfully applied to the determination of Sb(V) and Sb(III) in spiked natural water samples with good recoveries.

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Determination of Chromium (III) in Water Samples Using Continuous-Flow Microextraction With Graphite Furnace Atomic Absorption Spectrometry

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INTRODUCTION

Chromium is an essential element for all vertebrates and appears to play a role in the metabolism of glucose and some lipids such as cholesterol (1–3). Chromium in natural waters exists mainly in two different oxidation states: Cr(III) and Cr(VI) (4). Excessive amounts of chromium, particularly the more toxic hexavalent chromium, are detrimental to human health as they may be related to the pathogenesis of some diseases such as skin allergies and gastrointestinal cancers (5). Monitoring of chromium in biological and environmental samples is of great importance for the control of nutritional deficiencies and to prevent toxicity due to occupational exposure.

Chromium in natural waters is normally present at the low $\mu\text{g L}^{-1}$ level. In many cases, separation and preconcentration techniques are required to determine chromium at the ultra-trace levels in natural waters, even when the most sensitive techniques are used as, for instance, electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS). The most widely used techniques for the separation and preconcentration of trace chromium include liquid-liquid extraction (LLE) (6, 7), co-precipitation (8), solid-phase extraction (SPE) (9, 10), and cloud point extraction (CPE) (11). LLE is one of the widely used precon-

ABSTRACT

A new method is proposed using continuous-flow microextraction (CFME) combined with graphite furnace atomic absorption spectrometry (GFAAS) for the determination of chromium (III) in water samples. One drop (4.0 μL) of 8-hydroxyquinoline (Oxine) dissolved in chloroform is injected into a glass chamber by a microsyringe and remained at the outlet tip of a PTFE connecting tube. The sample solution flows through the tube and glass chamber, the solvent drop interacts continuously with the sample solution, and Cr(III) is extracted into the drop and concentrated. After extracting for a period of time (10 minutes), the drop is retracted into the microsyringe and directly injected into the graphite furnace for GFAAS determination of Cr(III). Several factors affecting the extraction efficiency, such as solution pH, sample flow rate, drop volume and extraction time, were optimized. Under the optimized conditions, an enrichment factor of 32 was obtained, and the detection limit for Cr(III) was 45 ng L^{-1} . The relative standard deviation for seven replicate analyses of 10 ng mL^{-1} of Cr(III) was 5.7%. The proposed method was applied to the determination of trace chromium in water samples with satisfactory results.

tration and matrix isolation techniques in the determination of metal ions. Although it offers high reproducibility and high sample capacity, it is considered to be a time- and labor-consuming procedure, has the tendency for emul-

sion formation and poor potential for automation, and uses large amounts of hazardous and costly organic solvents.

Recently, efforts have been made to miniaturize the LLE extraction procedure by greatly reducing the solvent-to-aqueous phase ratio, leading to the development of the liquid-phase microextraction (LPME) methodology (12,13). LPME is based on the distribution effect of the analytes between a microdrop of extraction solvent at the tip of a microsyringe needle and the aqueous sample solution. The solvent drop is first exposed to the sample solution and the target analyte is then transferred from the sample matrix into the drop. After extracting for a prescribed period of time, the microdrop is retracted back into the microsyringe and transferred to the instrumentation for further analysis. LPME uses an inexpensive apparatus and virtually eliminates solvent consumption, and combines extraction, preconcentration, and sample introduction in one step. Since the method was first introduced by Liu and Dasgupta in 1996 (14), further studies have exploited the analytical application of LPME. However, this method was mainly applied in the determination of organic pollutants and drugs in environmental and biological samples (15–18). To our knowledge, no application of LPME in the separation and preconcentration of metal ions has been reported in the literature.

Continuous-flow microextraction (CFME) is a novel LPME method, which was first reported by Liu and Lee (19). In this method,

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the extraction solvent drop is injected into a glass chamber by a conventional microsyringe and remained at the outlet tip of a PTFE connecting tube. The sample solution flows through the tube and extraction glass chamber to waste, the solvent drop interacts continuously with the sample solution, and extraction proceeds simultaneously. Because the drop of solvent fully and continuously makes contact with the sample solution, this method could gain a higher concentration factor. Hu et al. (20,21) made minor modifications to the method and combined it with low temperature electrothermal vaporization inductively coupled plasma atomic emission spectrometry/mass spectrometry (ICP-AES/MS) for the determination of trace elements.

The aim of this work is to combine CFME with GFAAS and develop a new method for the determination of trace chromium in water samples. 8-hydroxyquinoline (Oxine) dissolved in chloroform was used as the extraction solvent. Factors affecting the extraction efficiency, such as solution pH, sample flow rate, drop volume and extraction time, were studied and optimized.

EXPERIMENTAL

Instrumentation

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, P.R. China) was used, equipped with a deuterium background corrector and a GFH990 graphite furnace atomizer. All measurements were performed using integrated absorbance (peak area). A hollow cathode lamp for Cr was operated at 2 mA. The optimum operating parameters for GFAAS are given in Table I. CFME extraction was performed in a homemade glass chamber (~0.2 mL). A Model 2232 Microperpeps peristaltic pump (Pharmacia LKB, Upsalla,

Sweden) and a 10- μ L gas chromatography microsyringe (Shanghai, P.R. China) were used for delivery of the sample solution and introduction of the extraction solvent. A minimum length of PTFE tube (i.d. 0.5 mm) was used for all connections. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co., Ltd., Shanghai, P.R. China) supplied with a combined electrode.

Reagents and Solutions

Stock standard solution (1.000 g L⁻¹) of Cr(III) was prepared by dissolving CrCl₃·6H₂O in 0.1 mol L⁻¹ hydrochloric acid. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A 0.05M solution of 8-hydroxyquinoline (Oxine) was prepared by dissolving appropriate amounts of this reagent in chloroform from the commercially available product. All other reagents were of analytical reagent grade or better. Doubly distilled water made with a MYQ sub-boiling distilling water purification system (Changsha, P.R. China) was used throughout the entire study. The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with

doubly distilled water.

General Procedures

The schematic of the continuous-flow microextraction system used in this work is shown in Figure 1. The CFME consists of four steps:

- The aqueous sample was pumped continuously vertically upward and at a constant flow rate into the bulb glass extraction chamber (~0.2 mL) via the connecting PTFE tubing.
- After the chamber was filled with the sample solution, 4.0 μ L of Oxine-chloroform solution was introduced into the extraction chamber with a 10- μ L GC microsyringe. At this point, a drop forms

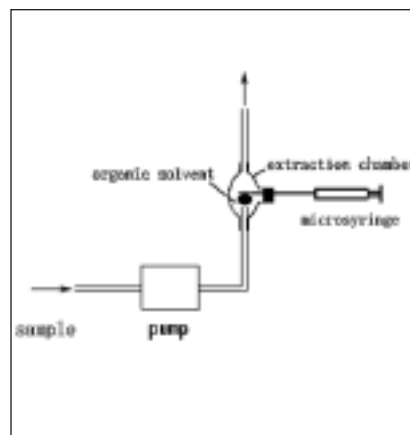


Fig. 1. Schematic of continuous-flow microextraction system.

TABLE I
Operating Parameters for GFAAS

Parameters	
Lamp Current	2.0 mA
Wavelength	357.9 nm
Slit	0.4 nm
Ar Flow Rate	200 mL min ⁻¹ (stopped during atomization)
Sample Volume	4 μ L
Temperature Program	
Drying	120 °C (Ramp 18 s, Hold 15 s)
Ashing	700 °C (Ramp 10 s, Hold 20 s)
Atomizing	2200 °C (Ramp 0 s, Hold 4 s)
Cleaning	2400 °C (Ramp 1 s, Hold 3 s)

which remains at the tip of the microsyringe above the PTFE tube outlet in extraction chamber.

(c) As the solvent drop is immersed in the sample solution, the analyte is extracted into the solvent drop from the sample solution, with the sample solution being continuously ejected from the PTFE tubing into the chamber.

(d) After extracting for a prescribed period of time (10 min), the solvent drop is retracted into the microsyringe and injected into graphite furnace for GFAAS determination.

Calibration was performed against aqueous standards submitted to the same CFME procedure. A blank submitted to the same procedure described above was measured in parallel to the samples and calibration solutions.

RESULTS AND DISCUSSION

Effect of pH

The pH plays a unique role on metal chelate formation and CFME extraction, so the effect of pH of the sample solution on the CFME extraction of Cr(III) was studied and the results are shown in Figure 2. It can be seen that the maximum absorbance of Cr(III) is obtained when a pH of 3 is applied. Accord-

ingly, a pH of 3 was selected for the subsequent work and the real water samples analysis. In order to avoid the change of Cr(III) to Cr(VI), HCl instead of HNO_3 was used to adjust the pH of the sample solution.

Flow Rate of Sample Solution

In CFME, the flow rate of the sample solution could affect the extraction dynamics remarkably since the thickness of the interfacial layer surrounding the drop will vary with the change of flow rate, which will affect the mass transfer of the analytes in both phases involved in the extraction. The effect of sample flow rate was evaluated using a flow rate ranging from 0.1 to 0.8 mL min^{-1} and the results are shown in the Figure 3. As can be seen, the absorbance of Cr(III) increased with the sample flow rate up to 0.4 mL min^{-1} . Reduction in absorbance was observed for Cr(III) after the flow rate exceeded 0.4 mL min^{-1} . This is possibly due to the linear velocity of the sample solution being too high to allow the establishment of extraction equilibrium in the interfacial layer of both phases. Therefore, a flow rate of 0.4 mL min^{-1} was used for subsequent work.

Solvent Drop Volume

In CFME, the volume of extraction solvent greatly affects the extraction efficiency. The influence of solvent drop volume on extraction efficiency of Cr(III) was investigated in the range of 1–5 μL with an extraction time of 10 minutes at a sample flow rate of 0.4 mL min^{-1} , and the result is shown in Figure 4. As can be seen, the absorbance of Cr(III) increased with the organic solvent volume up to 4.0 μL , then decreases slightly. On the other hand, the drop became too unstable to suspend at the needle tip when the volume exceeded 5.0 μL . Thus, a drop volume of 4.0 μL was selected for subsequent experiments.

Extraction Time

The effect of extraction time on the extraction efficiency was investigated from 2–15 minutes with a solvent drop volume 4.0 μL at a constant flow rate of 0.4 mL min^{-1} . The absorbance of Cr(III) increased with extraction time, but a long extraction time could lead to a high preconcentration factor and may also result in organic drop dissolution and poor precision. On basis of these facts, an extraction time of 10 minutes was selected for subsequent experiments.

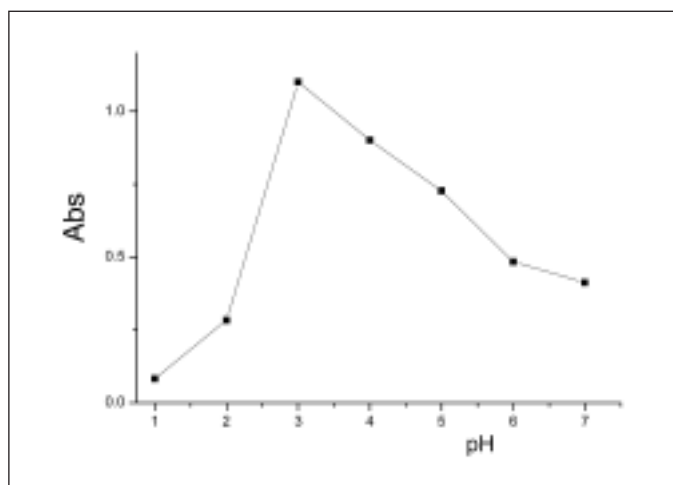


Fig. 2. Effect of pH on the CFME extraction of Cr(III).

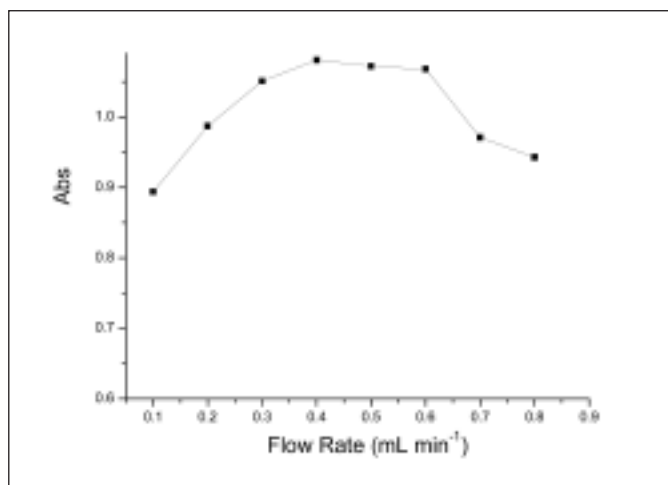


Fig. 3. Effect of flow rate on the CFME extraction of Cr(III).

TABLE II
Tolerance Limits of Coexisting Ions

Coexisting Ions	Foreign Ion-to-Analyte Ratio
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺	10,000
Al ³⁺ , Ba ²⁺	1,000
Cu ²⁺ , Co ²⁺ , Zn ²⁺	100
Cd ²⁺ , Ni ²⁺ , Mn ²⁺ , Pb ²⁺	50
Fe ³⁺	10

TABLE III
Determination of Cr(III) in Natural Water Samples

Samples	Added (μg L ⁻¹)	Found (μg L ⁻¹)	Recovery (%)
Tap Water	0	2.6	
	5	7.7	102
	10	12.5	99
Lake Water	0	11.2	
	5	16.0	96
	10	20.9	97

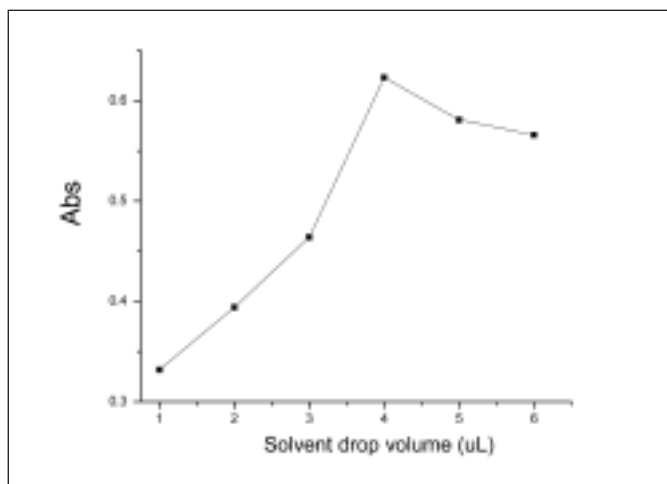


Fig. 4. Effect of solvent drop volume on the CFME extraction of Cr(III).

Interferences

The potential of interferences in the present system was investigated. Interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with Cr(III). The tolerable limit was taken as a relative error of $\leq \pm 5\%$. The tolerable concentration ratio of foreign ions to 10 ng mL⁻¹ Cr(III) was studied and the results are listed in Table II. As can be seen, large amounts of alkaline and alkaline earth metal ions show no interference with the microextraction of Cr(III) under the selected conditions because of their very low stability constants of Oxine complexes.

Evaluation of Method Performance

For the purpose of quantitative analysis, a calibration curve for Cr(III) with concentrations ranging over four orders was obtained by spiking the standards directly into distilled water and extracting under optimal conditions. Linearity was

observed over the range of 0–80 ng mL⁻¹ with a correlation coefficient (R^2) of 0.9994. The limit of detection (LOD) for Cr(III), based on a signal-to noise ratio (S/N) of 3, was 45 ng L⁻¹. The precision of this method was determined by analyzing a standard solution at 10 ng mL⁻¹ of Cr(III) for seven times in sequence, resulting in a relative standard deviation (RSD%) of 5.7%. The concentration factor (CF), defined as the ratio of the peak area of Cr(III) attained after and before CFME extraction, was 32.

Real Water Samples Analysis

In order to demonstrate the performance of the proposed method, tap water from our laboratory and a natural water sample from the East Lake of Wuhan were analyzed for Cr(III) presence. All water samples were filtered through a 0.45-mm membrane filter and analyzed as soon as possible. In addition, recovery experiments for different amounts of chromium(III) were carried out. The results in Table III

indicate that the recoveries were reasonable for trace analysis ranging from 96–102%.

CONCLUSION

A new continuous-flow microextraction (CFME) method coupled with GFAAS was developed for the determination of chromium(III) in water samples at the low ng mL⁻¹ level. The various parameters that affect the efficiency of CFME were optimized. The method is not only simple, virtually solvent-free, and low cost, but also proved to be stable, reliable, and accurate. The extraction time of the method is shorter than the common LPME method. The optimized procedure revealed satisfactory precision with a %RSD of 5.7% and the limit of detection was 45 ng L⁻¹. If the sample contains both oxidation states of chromium, reducing agent could be added to convert Cr(VI) to Cr(III), then the total Cr could be determined by the proposed method. As discussed above, this microextraction technique has great potential in trace element analysis.

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Extraction of Chromium, Copper, and Cadmium in Environmental Samples Using Cross-linked Chitosan-bound FeC nano-particles as Solid-phase Extractant and Determination by Flame Atomic Absorption Spectrometry

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INTRODUCTION

The accurate determination of trace elements in environmental and biological samples is an important and challenging task in analytical chemistry. Heavy metals are often monitored in environmental and biological samples (1-5). Nevertheless, the accurate determination of trace metals in many natural samples is extremely difficult because of the low concentration of these metals in a complex matrix. For this reason, an efficient separation and pre-concentration technique is frequently required.

A number of separation/pre-concentration methods have been used for trace metal determinations. These include precipitation/co-precipitation (6), liquid-liquid extraction (7,8), capillary micro-extraction (CME) (9,10), and solid-phase extraction (SPE) (11,12). Among these techniques, the SPE/CME techniques are superior to other procedures in terms of simplicity, consumption of small fractions of organic solvent, and the ability to obtain a higher enrichment factor (11,12). In the SPE technique, the extractant plays a fundamentally important role, and to develop an extractant (11,12) with the possibility of extracting a large number of elements over a wide pH range, fast and quantitative sorption and elution, high capacity, regenerability, and accessibility is always interesting to analysts. Numerous substances, such as

ABSTRACT

Cross-linked chitosan-bound FeC nano-particles (CCBFeCNP) were prepared, and the adsorptive behavior of Cr(III), Cu(II), and Cd(II) on CCBFeCNP was assessed. At pH 7.5, CCBFeCNP is selective towards Cr(III), Cu(II), and Cd(II). The retained Cr(III), Cu(II), and Cd(II) was subsequently eluted with 0.5 mol L⁻¹ HCl. A new method of flow injection (FI) using a micro-column packed with CCBFeCNP as solid-phase extractant has been developed for the determination of Cr(III), Cu(II), and Cd(II) in environmental samples, followed by flame atomic absorption spectrometry (FAAS). The effects of pH, sample flow rate and volume, elution solution and interfering ions on the recoveries of Cr(III), Cu(II), and Cd(II) were systematically investigated. Under optimum conditions, the adsorption capacities of CCBFeCNP for Cr(III), Cu(II), and Cd(II) were 10.5, 17.8, and 20.3 mg g⁻¹, respectively. The procedure presented was successfully applied to the determination of Cr(III), Cu(II), and Cd(II) in environmental samples, and the results were satisfactory.

modified silica (13), alumina (14), C60-NaDDC (15), cellulose (16), nanometer-sized material (17), and chelating resins (12) have been proposed and investigated with the development of SPE.

The field of nano-composite materials has attracted the attention, imagination, and scrutiny of scientists and engineers in recent years (18-24). Compared to the

traditional micron-sized supports used in the separation process, nano-sized carriers possess quite good performance due to a high specific surface area and the absence of internal diffusion resistance (18-21). Recently, Chang et al. found that the chitosan-bound Fe₃O₄ nano-particles were shown to be quite efficient for the removal of Cu(II) ions (25) at pH >2, and Co(II) ions (26) at pH 3-7, with fast adsorption equilibrium. By using nano-particles, Gao et al. (27) determined partition coefficient values of organic compounds in noctanol/water. In addition, Wu et al. (28) reported that most of the brilliant blue FCF (BBF) dye is adsorbed and desorbed within 15 minutes on the organosilane-functionalized Fe₃O₄ composite particles.

All of the facts mentioned above reveal to us that nano-particles containing Fe compounds may have great analytical potential as a solid-phase extractant for extraction of Cr(III), Cu(II), and Cd(II) in environmental samples. However, so far there has been no report of its application as adsorbent for environmental samples. In this work, using FeC nano-particles as cores, an epichlorohydrin cross-linked chitosan-bound FeC nano-particle (CCBFeCNP) was prepared, and the analytical potential of CCBFeCNP as adsorbent for the extraction of Cr(III), Cu(II), and Cd(II) was assessed. This method, using a micro-column packed with CCBFeCNP as adsorbent, has been developed for the extraction of Cr(III), Cu(II), and Cd(II) in environmental samples prior to their determination by FAAS.

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EXPERIMENTAL

Instrumentation

The determination of metal ion concentrations was performed on a WFX-110 atomic absorption spectrometer (Beijing Rayleigh Analytical Instrument Company, Beijing, P.R. China) by using an air-acetylene flame. A Model HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, P.R. China) was used in the separation and pre-concentration process. The pH values were controlled with a PHS-25 pH meter (Shanghai Exact Science Instruments Co. LTD., P.R. China) supplied with a combined electrode. The pH meter was calibrated against two standard buffer solutions of pH 4.0 and 7.0. All instrumental parameters were used as recommended by the manufacturers.

A minimum length of PTFE tubing (i.d. 0.5 mm) was used for FI connections. A self-made PTFE micro-column (20 mm \times 3.0 mm i.d.) was used.

Standard Solutions and Reagents

Stock solutions (1 g L⁻¹) of Cr(III), Cu(II), and Cd(II) were prepared from high-purity CrCl₃·6H₂O and CuCl₂ (The First Reagent Factory, Shanghai, P.R. China), and stock solutions (1 g L⁻¹) of Cd(II) were prepared by dissolving Cd(NO₃)₂ (purity >99.99%) in 0.1 mol L⁻¹ HNO₃. Analytical standard solutions of metals were prepared by diluting the stock solutions.

Biochemicals: Chitosan (Shanghai Boao Biological Science and Technology Co. LTD., P.R. China). The size of nano-particle FeC (Shenzhen Zunye Nano-sized Material Co. LTD., P.R. China) was approximately 25 nm. Britton–Robinson (B-R) buffer solution was used to adjust the pH, which was composed of an appropriate vol-

ume of 0.04 mol L⁻¹ H₃PO₄ – 0.04 mol L⁻¹ HAc – 0.04 mol L⁻¹ H₃BO₃ and 0.2 mol L⁻¹ NaOH.

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout.

Preparation of CCBFeCNP

The preparation method is similar to the procedure reported by Yuan and coworkers (29). Firstly, two phases were prepared: Organic phase, 15 mL of paraffin was mixed with 5 mL of Span-80 (a non-ionic surfactant); water phase, 20 mL of 2.5% chitosan in 3% HAc (v/v) solution was mixed with 0.5 g of FeC nano-particles. Secondly, the water phase was added into the organic phase in drops at the stirring rate of 1500 r min⁻¹. After reaction for 30 minutes at room temperature at the stirring rate of 2000 r min⁻¹, the pH of the mixture was adjusted to 10 with 1.0 mol L⁻¹ NaOH (containing 10% NaBH₄ solution) at the stirring rate of 1200 r min⁻¹. Thirdly, 0.3 mL of epichlorohydrin was added and reacted within 40 minutes at the temperature of 40 °C. Then, 0.3 mL of epichlorohydrin was added again and the stirring rate lowered to 1000 r min⁻¹ for one hour. Then the stirring rate was lowered to 800 r min⁻¹ and kept at 60–70 °C for 2 hours. After cooling, the solid was separated magnetically, rinsed with ether, acetone, 10% ethanol, doubly distilled water, and vacuum-dried at 50 °C prior to storage for later use.

Column Preparation

A total of 50 mg of CCBFeCNP was filled into a PTFE micro-column (20 mm \times 3.0 mm i.d.), plugged with a small portion of glass wool at both ends. The column was conditioned to the desired pH with B-R buffer solution.

General Procedure

A 10-mL portion of aqueous sample solution containing Cr, Cu, and

Cd was prepared, and the pH was adjusted to the desired value with B-R buffer solution. The solution was passed through the column at a flow rate of 1.5 mL min⁻¹ by using a peristaltic pump. Afterwards, the metal ions retained on the micro-column were eluted with 1.0 mL of 0.5 mol L⁻¹ HCl at a flow rate of 1.0 mL min⁻¹. The analytes in the elution were determined by FAAS. The column could be used repeatedly after regeneration with 0.2 mol L⁻¹ NaOH solution and distilled water, respectively. The recommended procedure was used throughout the different tests that follow.

RESULTS AND DISCUSSION

Particle Morphologies of CCBFeCNP

The adsorption characteristics of a material are related to its physical morphology; thus, the particle morphology of CCBFeCNP is an important factor affecting its performance. Figure 1 shows the morphologies of CCBFeCNP characterized by transmission electron microscopy (TEM), which was performed on a JEOL-2010 FEF microscope (200 V) using copper grids.

Effect of pH on Adsorption

The effect of pH on the retention of Cr, Cu, and Cd on the column of CCBFeCNP was investigated. In order to evaluate the effect of pH, the pH values of the sample solutions were adjusted ranging from 2.0 to 9.0 with B-R buffer solution. The results of the effect of pH on the recoveries of Cr, Cu, and Cd are shown in Figure 2. It can be seen that Cu and Cd were absorbed poorly at a pH of less than 5. Quantitative recoveries (over 90%) for Cr, Cu, and Cd were obtained in the pH range of 7.0–9.0. Thus, a pH of 7.5 was selected as the compromise condition.

Effect of Flow Rates of Sample Solutions

Since the retention of the analytes on the adsorbent depends on the flow rate of the sample solution, the effect of the sample flow rate was examined under the optimum pH (7.5) by passing the sample solution through the micro-column with the flow rates ranging from 0.5 ~ 2.5 mL min⁻¹. The results of the effect of pH on the recoveries of the studied ions are shown in Figure 3. It can be seen that quantitative recoveries of Cr, Cu, and Cd were obtained at flow rates of less than 1.5 mL min⁻¹. The recoveries of Cr, Cu, and Cd will decrease with an increase in the flow rate from 0.5 to 2.5 mL min⁻¹ due to a decrease in the adsorption kinetics at a high flow rate. Thus, a flow rate of 1.5 mL min⁻¹ was employed in this work.

Effect of Desorption Condition

With respect to stripping of Cr, Cu, and Cd from CCBFeCNP, 1.0 mL of HCl was employed and different concentrations of HCl were studied for the elution of Cr, Cu, and Cd retained in the micro-column at a flow rate of 1.0 mL min⁻¹. The results obtained are

given in Table I. As can be seen, 0.5 mol L⁻¹ HCl is sufficient for complete elution. The effect of eluent volume on the recoveries of the analytes was also studied by keeping the HCl concentration at 0.5 mol L⁻¹. It was found that quantitative recoveries (over 90%) could be obtained with 1.0 mL of 0.5 mol L⁻¹ HCl. Therefore, 1.0 mL of 0.5 mol L⁻¹ HCl was used for the following experiments.

The effect of desorption flow rate was examined at a flow rate of 0.5~2.5 mL min⁻¹ with 1.0 mL of 0.5 mol L⁻¹ HCl. The results are given in Figure 4. It was shown that the recoveries of Cr, Cu, and Cd strongly depended on the eluent flow rate; the higher the flow rate of HCl, the lower the recoveries of Cr, Cu, and Cd. When the flow rate was controlled within 0.5~1.0 mL min⁻¹, the recoveries of Cr, Cu, and Cd were over 90%. Therefore, a desorption flow rate of 1.0 mL min⁻¹ was selected in this work.

Effect of Sample Volume

In order to explore the possibility of enriching low concentrations of analytes from large volumes, the maximum applicable sample vol-

ume must be determined. For this purpose, 10, 25, 50, and 100 mL of sample volume were adopted to test the effect of sample volume. Sample solutions containing 2.0 µg Cr, Cu, and Cd at pH 7.5 were passed through the micro column at the optimum flow rate and the results are listed in Table II. It can be seen that quantitative recoveries (over 90%) were obtained with sample volumes less than 100 mL for Cr, Cu, and Cd. As described previously, 1.0 mL of 0.5 mol L⁻¹ HCl was enough to elute the analyte adsorbed in the micro column. An enrichment factor of 100 was obtained with 100 mL of sample solution. This proves that samples with different analytes concentration levels can be analyzed.

Adsorption Capacity

The adsorption capacity is an important factor to evaluate CCBFeCNP, because it determines how much CCBFeCNP is required to quantitatively concentrate the analytes from a given solution. Under optimum conditions, the determination of dynamic adsorption capacity of a pure metal was performed based on the procedure recommended by Maquieira (30) where 25-mL aliquots of a series of

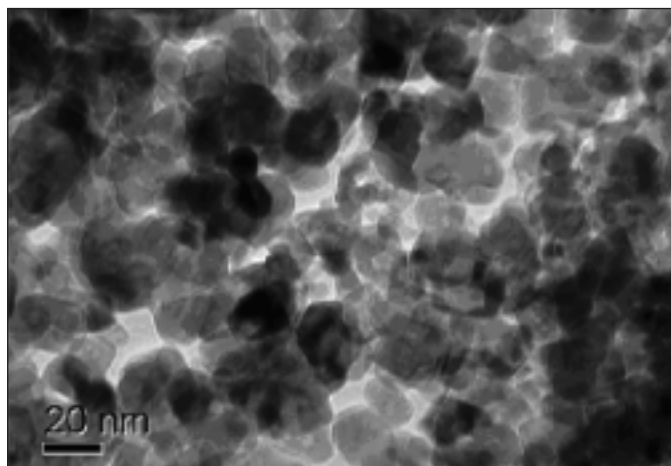


Fig. 1. Transmission electron microscopy of coating performed on a JEOL-2010 FEF microscopy (200V) using copper grids.

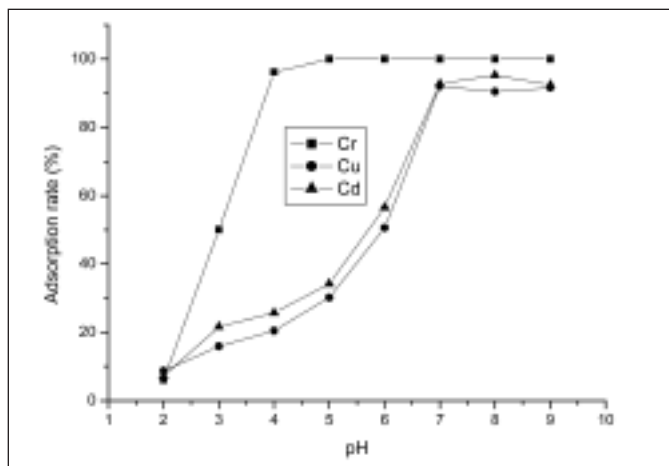


Fig. 2. Effect of pH on the adsorption of the studied metal ions on CCBFeCNP; Cr, Cu and Cd: 0.5 mg L⁻¹.

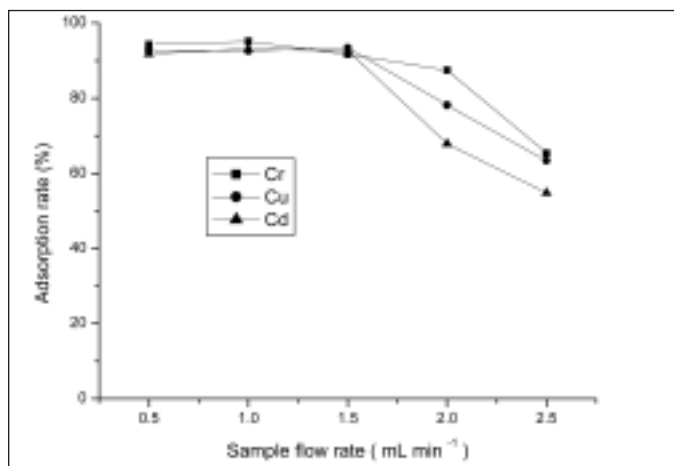


Fig. 3. Effect of flow rates of sample solutions; Cr, Cu and Cd: 0.5 mg L⁻¹.

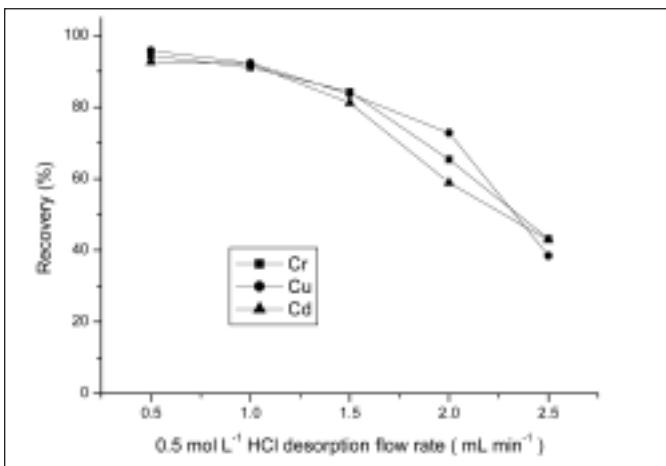


Fig. 4. Effect of 1.0 mL 0.5 mol L⁻¹ HCl desorption flow rate; Cr, Cu and Cd: 0.5 mg L⁻¹.

TABLE I
Recoveries (%) With Different HCl Elution

Eluent (HCl)/mol L ⁻¹	Cr	Cu	Cd
0.05	54.7	77.5	81.9
0.1	79.8	94.2	96.2
0.5	91.4	93.2	95.1
1.0	95.2	94.1	96.7
1.5	93.8	95.7	95.4

TABLE II
Effect of Sample Volume on the Recovery (%) of Cr, Cu, and Cd

Sample Volume (mL)	Cr	Cu	Cd
100	91.8	90.6	91.4
50	92.5	90.8	90.2
25	90.1	91.5	93.3
10	92.3	90.6	92.8

TABLE III
Effect of Interfering Ions on the Determination of 0.5 mg L⁻¹ Cr, Cu, and Cd

Interfering Ions	Concentration (μg mL ⁻¹)	Recovery (%)		
		Cr	Cu	Cd
K ⁺	5000	90.6	95.2	91.2
Ca ²⁺	1000	91.7	93.4	93.5
Na ⁺	5000	92.0	94.0	92.6
Mg ²⁺	3000	90.0	96.0	102.0
F ⁻	1000	92.0	101.0	90.7
SO ₄ ²⁻	500	91.0	92.0	92.2
H ₂ PO ₄ ⁻	500	91.3	93.8	91.8

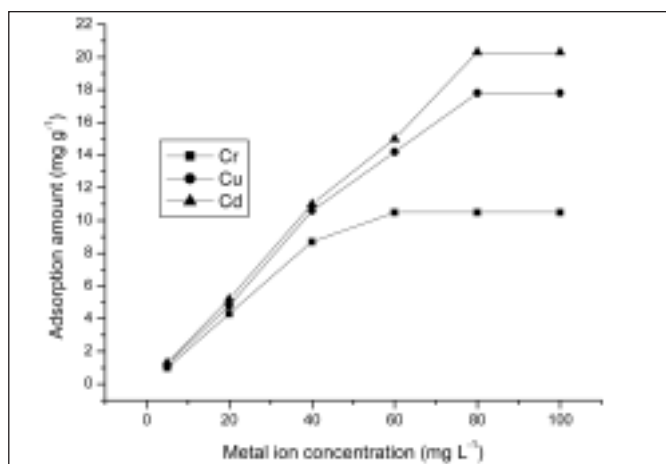


Fig. 5. Breakthrough curve of the studied metal ions on CCBFeCNP; pH: 7.5; sample volume: 25 mL.

concentrations (5 – 100 mg mL⁻¹) of a pure metal solution were adjusted to the appropriate pH, respectively, then analyzed according to the general procedure described previously. A breakthrough curve was obtained by plotting the total Cr, Cu, and Cd concentration (mg mL⁻¹) versus the Cr, Cu, and Cd adsorbed per gram (mg g⁻¹) (see Figure 5), respectively. The adsorption capacity of a pure metal evaluated from the breakthrough curve was 10.5,

17.8, and 20.3 mg g⁻¹ CCBFeCNP for Cr, Cu, and Cd, respectively.

Interferences of Coexisting Ions

The effects of foreign ions on the adsorption of Cr, Cu, and Cd on CCBFeCNP were investigated. In these experiments, solutions of 0.5 mg L⁻¹ of Cr, Cu, and Cd containing the added interfering ions were treated according to the recommended procedure. The results are shown in Table III. The effect was expressed as the recovery in the presence of interfering ions relative to the interference-free response. As can be seen, 5 mg mL⁻¹ Na⁺, K⁺; 1 mg mL⁻¹ Ca²⁺; 3 mg mL⁻¹ Mg²⁺; 1.0 mg mL⁻¹ F⁻; and 0.5 mg mL⁻¹ H₂PO₄⁻ and SO₄²⁻ have no obvious influence on the separation or determination of Cr, Cu, and Cd under the selected conditions.

Regeneration and Stability of the Column

The stability and potential regeneration of the column were investigated. The column can be re-used after regeneration with 10 mL of 0.2 mol L⁻¹ NaOH and 10 mL of distilled water. It is stable for up to 15 adsorption-elution cycles without obvious decrease in the recoveries for the studied ions.

Analytical Performance

The detection limits (evaluated as the concentration corresponding to three times the standard deviation of 9 runs of the blank solution) of this method for Cr, Cu, and Cd with an enrichment factor (EF) of 100 were 52.4, 60.2, and 55.7 ng L⁻¹, respectively; and the relative standard deviations (RSDs) were 2.5%, 4.2%, and 3.0%, respectively (n = 9, c=20 ng mL⁻¹). For comparison of the analytical characteristics of this method, the figures of merit of various methods for the extraction of Cr, Cu, and Cd using column preconcentration are listed in Table IV. As can be seen, the LODs and the enrichment factor of this method are superior to most of the other methods (31–34).

Analytical Application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of studied elements (Cr, Cu, and Cd) in a standard reference material (GBW07605 Tea Leaves). A 0.30 g amount of GBW07605 Tea Leaves was weighed and dissolved in 20 mL of HNO₃-HClO₄ (4:2, v/v) on a hot plate under mild heating and vaporized to near dryness, then finally dissolved in 10 mL of a pH 7.5 B-R buffer solution. The content of the

studied elements was determined according to the recommended procedure. The results are presented in Table V. As can be seen, the results obtained are in good agreement with the reference values.

The proposed method was applied to the determination of Cr, Cu, and Cd in a natural lake water sample (Qingshan Lake, Huangshi, P.R. China), and the spike recoveries of spiked of the studied ions were determined. The collected lake water sample was filtered through a 0.45-μm membrane filter and analyzed as soon as possible after sampling. The analytical results and the recoveries are given in Table VI. The results indicate that the recoveries are reasonable for trace analysis, ranging from 91.0–103.0 %.

CONCLUSION

The adsorption behavior of Cr, Cu, and Cd on cross-linked chitosan-bound FeC nano-particles (CCBFeCNP) was studied systematically and found to be 20.5, 17.8, and 20.3 mg g⁻¹, respectively. The method is simple, sensitive, and selective for the extraction and determination of these elements in environmental samples using CCBFeCNP as solid-phase extrac-

TABLE IV
Figures of Merit of Methods for Extraction of Cr, Cu, and Cd Using Column Preconcentration

Matrix	Analyte Retained by the Column	Preconcentration Material and Enrichment Factor	LOD	Detection Technique	Ref.
Lake Water	Cr, Cu, and Cd	CCBFeCNP (EF 100)	52.4 – 60.2 ng L ⁻¹	FAAS	This work
Natural Water Samples	13 trace metals, including Be, Cd, Cr, Cu and Pb	Iminodiacetate chelating resin (EF 19)	0.001 – 0.18 ng mL ⁻¹	AES	31
Waters, Rice, and Coal Samples	Cd/Cr/Cu/Pb -alphanbenzoin oxime complex	Diaion SP-850 resin (EF 50)	0.30 – 0.65 ng mL ⁻¹	AAS	32
Lake Water	Cd, Cr, Cu, and Mn	Immobilized nanometer TiO ₂ (EF 50-150)	21 – 48 ng L ⁻¹	AES	33
Water and Sediments	Cr(VI) - APDC complex	Polytetrafluoroethylene (PTFE) turnings (EF80)	0.8 ng mL ⁻¹	AAS	34

TABLE V
The Analytical Results of Standard Reference Material (GBW07605 Tea Leaves) ($\mu\text{g g}^{-1}$)

Element	Reference Value	Found ^a
Cr	0.80 ± 0.02	0.75 ± 0.03
Cu	17.3 ± 1.0	16.5 ± 1.2
Cd	0.057 ± 0.008	0.064 ± 0.006

^a The value following “ \pm ” is the standard deviation ($n = 3$).

tion adsorbent. The precision and accuracy of the method is satisfactory. The method may be used for the determination of Cr, Cu, and Cd in various matrices other than environmental samples.

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TABLE VI
Determination of Metal Ions in Lake Water (ng mL^{-1})

Element	Added	Found	Recovery (%)
Cr	0	6.5	-
	10.0	15.8	93.0
	20.0	27.1	103.0
Cu	0	12.8	-
	10.0	21.9	91.0
	20.0	31.2	92.0
Cd	0	1.4	-
	10.0	11.5	101.0
	20.0	20.7	96.5

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Direct and Simultaneous Determination of As, Cu, and Pb in Brazilian Sugar Cane Spirits by Graphite Furnace AAS Using Tungsten Permanent Modifier With Co-Injection of Pd/Mg(NO₃)₂

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ABSTRACT

A method was developed using the multi-element graphite furnace atomic absorption spectrometry technique for the direct and simultaneous determination of As, Cu, and Pb in Brazilian sugar cane spirit (cachaça) samples. Also employed was the end-capped transversely heated graphite atomizer (THGA) with platforms pre-treated with W permanent modifier and co-injection of Pd/Mg(NO₃)₂. Pyrolysis and atomization temperature curves were established in a cachaça medium (1+1; v/v) containing 0.2% (v/v) HNO₃ and spiked with 20 µg L⁻¹ As and Pb and 200 µg L⁻¹ Cu. The effect of the concentration of major elements usually present in cachaça matrices (Ca, Mg, Na, and K) and ethanol on the absorbance of As, Cu, and Pb was investigated. Analytical working solutions of As, Cu, and Pb were prepared in 10% (v/v) ethanol plus 5.0 mg L⁻¹ Ca, Mg,

Na, and K. Acidified to 0.2% (v/v) HNO₃, these solutions were suitable to build calibration curves by matrix matching. The proposed method was applied to the simultaneous determination of As, Cu, and Pb in commercial sugar cane spirits. The characteristic mass for the simultaneous determination was 16 pg As, 119 pg Cu, and 28 pg Pb. The pretreated tube lifetime was about 450 firings. The limit of detection (LOD) was 0.6 µg L⁻¹ As, 9.2 µg L⁻¹ Cu, and 0.3 µg L⁻¹ Pb. The found concentrations varied from 0.81 to 4.28 µg L⁻¹ As, 0.28 to 3.82 mg L⁻¹ Cu and 0.82 to 518 µg L⁻¹ Pb. The recoveries of the spiked samples varied from 94–112% (As), 97–111% (Cu), and 95–101% (Pb). The relative standard deviation (n=12) was 6.9%, 7.4%, and 7.7% for As, Cu, and Pb, respectively, present in a sample at 0.87 µg L⁻¹, 0.81 mg L⁻¹, and 38.9 µg L⁻¹ concentrations.

inorganic elements, but a few contaminants such as Pb and As may be found at lower concentrations. For trade market reasons, the maximum allowable levels of As, Cu, and Pb were set at 0.1 mg L⁻¹, 5 mg L⁻¹, and 0.2 mg L⁻¹, respectively, for Brazilian cachaça by the Brazilian Ministry of Agriculture, Livestock, and Food Supply (7).

Among the main analytical techniques employed for the determination of inorganic trace metals in an alcoholic matrix are atomic absorption (5,8–9) and mass (10–11) spectrometry. Inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) are the most sensitive techniques for trace metals analysis. ICP-MS instrumentation has the capability for multi-elemental and isotopic determinations but is very expensive, requires highly skilled analysts, and is thus out of reach for the general laboratory. GFAAS, on the other hand, is a more simple technique, well-established, exhibits high selectivity and sensitivity, and is easily adjustable for solid sampling (2,12–14). However, matrix interferences of special samples, such as fuel ethanol (15) and cachaça (2,9,14), limit the application of GFAAS. These drawbacks may be circumvented by using standard addition (8,16) or matrix matching (17–18) as the calibration method.

Little attention has been given in the literature to the development of methods for the direct and simultaneous determination of As, Cu, and Pb in cachaça by GFAAS. This study

INTRODUCTION

Brazilian sugar cane spirit (cachaça) is a distilled beverage produced by fermentation of sugar cane and appreciated by people around the world (1–3). The annual production of cachaça is around 2 billion liters, representing U.S. \$2.5 billion for this agribusiness activity. Knowledge of the

chemical composition of cachaça has improved over the years (4–5), so that producers can successfully control the sensory profile and ensure high quality of the final product.

The chemical composition of cachaça is relatively complex. Among the main organic substances usually found is ethanol, varying from 38–48% (v/v). Minor compounds such as higher alcohols, acids, esters, aldehydes, and ketones delineate the bouquet of the beverage (6). Calcium, Cu, Fe, Mg, K, and Na are the main

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reports a simple and fast method for the direct and simultaneous determination of As, Cu, and Pb in cachaça by GFAAS with a transversely heated graphite atomizer (THGATM, PerkinElmer) and longitudinal Zeeman-effect background correction. Tungsten as permanent modifier with co-injection of palladium + magnesium nitrate is proposed here to increase the THGA lifetime. The performance of the proposed method was checked by the analysis of commercial Brazilian sugar cane spirit samples.

EXPERIMENTAL

Instrumentation

All measurements were performed on a PerkinElmer SIMAATM 6000 simultaneous multi-element atomic absorption spectrometer, equipped with a transversely heated graphite atomizer (THGA), longitudinal Zeeman-effect background (BG) corrector, and an AS-72 autosampler (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The experiments were carried out under stabilized temperature platform furnace conditions (19–20). The platform of the end-capped graphite tube (PerkinElmer, Part Number B3000653) was coated with tungsten by using the facilities provided by the original software of the autosampler and graphite furnace. A mass of 250 µg W was thermally and sequentially deposited onto the integrated platform as described elsewhere (21–22). A PerkinElmer electrodeless discharge lamp for As (operated at 380 mA current) and a LuminaTM hollow cathode lamps of Cu (10 mA) and Pb (20 mA) were employed as the radiation sources. The spectral lines at 193.7 nm, 249.2 nm, and 283.3 nm were selected to measure As, Cu, and Pb, respectively, with a spectral band-pass of 0.7 nm. High purity argon (99.999%, White Martins, Brazil)

was used as the purge gas throughout at a flow rate of 250 mL min⁻¹. This flow was stopped during the atomization step. Other operating conditions were carried out according to the recommendations of the manufacturer.

Reagents, Analytical Solutions, and Samples

High purity water (resistivity 18.2 MΩ·cm), obtained by a Millipore Rios 5TM reverse osmosis and a Millipore Milli-Q AcademicTM deionizer system (Bedford, MA, USA), was used throughout the work. SuprapurTM nitric acid (Merck, Darmstadt, Germany) and anhydrous ethanol (99.9% P.A., J.T. Baker, Xalostoc, Mexico) were used to prepare the working standard solutions. The tungsten chemical modifier (1.00 g L⁻¹) was prepared by dissolving 0.1794 g of Na₂WO₄·2H₂O (Merck, Darmstadt, Germany) in 100 mL of deionized water. The 0.1% (m/v) Pd/Mg(NO₃)₂ chemical modifier solution was prepared by appropriate dilution of each 10.0 g L⁻¹ Pd(NO₃)₂ and Mg(NO₃)₂ stock solutions (Merck, Darmstadt, Germany).

For calibration, multi-elemental analytical working solutions were prepared daily by appropriate dilution of the 1000 mg L⁻¹ stock solutions of As, Cu, and Pb (Titrisol®, Merck, Darmstadt, Germany). Analytical working solutions (5.0, 10, 15, and 20 µg L⁻¹ As and Pb; 50, 100, 150, and 200 µg L⁻¹ Cu) were prepared in 10% (v/v) ethanol plus 5.0 mg L⁻¹ Ca, Mg, Na, and K and acidified to 0.2% (v/v) HNO₃ to build the calibration curves by matrix matching. For calibration, 5 µL of 0.1% (m/v) Pd plus 3 µL of 0.1% (m/v) Mg(NO₃)₂ and 20 µL of a blank or analytical solution were sequentially injected into the pre-heated graphite atomizer at 80 °C in order to obtain a faster drying step. For analysis of the samples, 5 µL of 0.1% (m/v) Pd, 3 µL of 0.1% (m/v) Mg(NO₃)₂, 10 µL of a solu-

tion containing 0.4% (v/v) HNO₃ + 20% (v/v) ethanol, and 10 mg L⁻¹ Ca, Mg, Na, K plus 10 µL of the samples were sequentially injected onto the graphite furnace platform. All measurements of integrated absorbance were made at least in triplicate.

The solution inside the autosampler reservoir was 0.2% (v/v) HNO₃. Brazilian sugar cane spirits were purchased at the local market in Araraquara, São Paulo State, Brazil, and analyzed without previous treatment. All solutions were stored in NalgeneTM high-density polypropylene flasks (Nalge Nunc International, Rochester, NY, USA). Plastic bottles, autosampler cups, and glassware were cleaned by soaking overnight in a 10% (v/v) HNO₃ solution and rinsing abundantly in de-ionized water before use.

Procedure

Since the concentration of Cu in cachaça is typically higher than those encountered for As and Pb, the absorbance measurements of As, Cu, and Pb were carried out at primary lines of As (193.7 nm) and Pb (283.3 nm), but at a secondary line for Cu (249.2 nm). The pyrolysis and atomization temperature curves were built in order to select the optimum pyrolysis and atomization temperatures for each analyte, taking into consideration the prerequisites for simultaneous detection. Since the heating program of the graphite tube is common for all analytes, the pyrolysis temperature should be as high as possible to guarantee matrix elimination; however, this temperature is limited by the most volatile element of the group. On the other hand, the atomization temperature should be as low as possible to avoid faster graphite tube deterioration, and this temperature is limited by refractory elements. The pyrolysis and atomization temperature curves were established in diluted

cachaça (1+1; v/v) containing 0.2% (v/v) HNO₃ and spiked with 20 µg L⁻¹ As and Pb and 200 µg L⁻¹ Cu. All measurements were carried out using three replicates. The influence of variation of concentration of Ca, Mg, K, Na, ethanol, and the mixture of them was evaluated by processing a solution containing 20 µg L⁻¹ As, Pb and 100 µg L⁻¹ Cu acidified to 0.2% (v/v) HNO₃ and comparing the respective absorbance with solutions containing:

- (a) Ca (0–20 mg L⁻¹);
- (b) K (0–20 mg L⁻¹);
- (c) Na (0–20 mg L⁻¹);
- (d) Mg (0–20 mg L⁻¹);
- (e) anhydrous ethanol (0–50% v/v),
- (f) Ca, K, Na, Mg (0–20 mg L⁻¹) plus anhydrous ethanol (0–20% v/v).

Plots of the integrated absorbance of As, Cu, and Pb versus concentration of foreign species were built up aiming to illustrate eventual interferences. After these studies, analytical solutions were prepared in the following diluents to verify the optimal analysis conditions:

- (a) 0.2% (v/v) HNO₃,
- (b) three diluted cachaça samples,
- (c) ethanol (10, 25 and 50%, v/v),
- (d) ethanol 10% (v/v) + 5 mg L⁻¹ Ca, Mg, Na and K, and
- (e) 5 mg L⁻¹ Ca, Mg, Na, and K.

In all procedures, the solutions were acidified to 0.2% (v/v) HNO₃.

Precision Study

After optimization of the parameters, the proposed procedure was applied to As, Cu, and Pb determination in 12 Brazilian commercial cachaça samples in order to assess the accuracy and precision of the method. In addition, analyte recovery tests were carried out in 10 cachaça samples spiked with 10 µg L⁻¹ As and Pb, and 100 mg L⁻¹ Cu.

RESULTS AND DISCUSSION

Optimization of the Graphite Furnace Conditions

Shown in Figure 1 are the pyrolysis and atomization temperature curves for As, Cu, and Pb employing W + Pd/Mg(NO₃)₂ as modifiers. The optimal pyrolysis and atomization temperatures were 1200 °C and 2100 °C, respectively. The optimized heating program of the graphite tube employed for the direct and simultaneous determination of As, Cu, and Pb in sugar cane spirits is illustrated in Table I. The pretreated tube lifetime was about 450 firings.

Interference Studies

Sodium, potassium, calcium, magnesium, and ethanol were tested as foreign species since they are the major chemical components of most cachaças. Figure 2 illustrates the influence of these interferences on the absorbance of As, Cu, and Pb. Calcium and sodium did not alter the absorbance of all analytes. Potassium at concentrations of >10 mg L⁻¹ interfered on the Pb and As signals. A slight reduction in arsenic absorbance was observed at magnesium concentrations of >10 mg L⁻¹. The effect of ethanol was more pronounced for the As signals at concentrations of >10% (v/v) ethanol. It should be pointed out

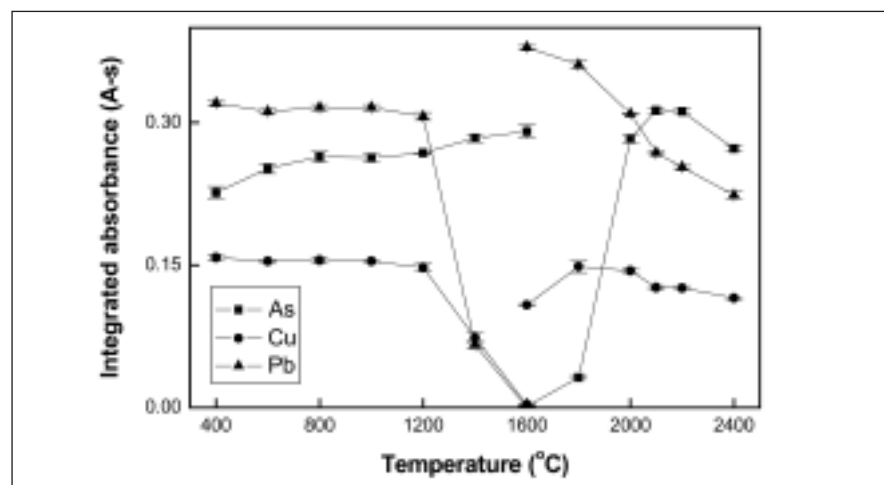


Fig. 1. Pyrolysis and atomization curves for 0.4 ng As and Pb, and 4.0 ng Cu in cachaça medium employing W + Pd/Mg(NO₃)₂ as chemical modifier.

TABLE I
Optimized Heating Program of the Graphite Tube for the Direct and Simultaneous Determination of As, Cu and Pb in Brazilian Sugar Cane Spirits

Step	Temp. (°C)	Ramp Time (s)	Hold Time (s)	Argon Flow Rate (mL min ⁻¹)
Drying 1	100	5	5	250
Drying 2	120	5	10	250
Pyrolysis	1200	10	30	250
Atomization	2100	0	5	0
Cleaning	2450	1	5	250

Injection temperature: 80°C

that for a solution containing either 5 mg L⁻¹ Na, K, Ca, or Mg in 10% (v/v) ethanol, no measurable alteration in analyte absorbance was observed. Thus, this ethanol solution was selected as the diluent for matrix-matched calibrations.

Matrix effects were evaluated by comparing the slopes of analytical curves (see Table II) prepared in the following media:

- (a) 0.2% (v/v) HNO₃,
- (b) three diluted cachaças (1+1, v/v),
- (c) 10%, 25% and 50% (v/v) of ethanol,
- (d) 10% (v/v) ethanol plus 5.0 mg L⁻¹ Ca, Mg, Na, and K, and
- (e) 5.0 mg L⁻¹ Ca, Mg, Na, and K.

The solutions above were acidified to 0.2% (v/v) HNO₃ and spiked with the analytes in order to produce calibration curves in the 0–20 µg L⁻¹ As and Pb, and 0–200 µg L⁻¹ Cu concentration ranges. The analysis of Table II reveals that calibration curves prepared in 0.2% (v/v) HNO₃ were inappropriate to determine As, Cu, and Pb simultaneously in the cachaça samples. The use of analytical solutions containing 10% (v/v) ethanol plus 5.0 mg L⁻¹ of Ca, K, Na, Mg in 0.2% (v/v) HNO₃ were effective to circumvent matrix effects for practically all samples analyzed. So this was the optimum diluent for calibration by matrix matching. Tungsten with co-injection of Pd/Mg(NO₃)₂ acted as an effective modifier for the simultaneous determination of As, Cu, and Pb in the cachaça matrix since similar atomization signals were obtained for the different samples. It should be stressed that although the mixture Pd/Mg(NO₃)₂ is proposed for the simultaneous determination of As and Cu in fuel ethanol (23), this modifier was not efficient for the cachaça samples, indicating that ethanol and cachaça represent significantly different matrices.

Analysis of Real Samples

For 20 µL of injected standard solutions in the 0–20 µg L⁻¹ As and Pb, and 0–200 µg L⁻¹ Cu concentration intervals, analytical curves were established and linear correlations of $r^2 > 0.999$, $r^2 > 0.997$, and $r^2 > 0.999$ were typically obtained for As, Cu, and Pb, respectively. Limits of detection (LODs) were calculated based on the standard deviation of 12 measurements of a blank solution prepared in nitric acid 0.2% (v/v) according to IUPAC regulations (24). The LOD was 0.6 µg L⁻¹ As, 9.2 µg L⁻¹ Cu, and 0.3 µg L⁻¹ Pb, and the relative stan-

dard deviations (n = 12) were 6.9%, 7.4%, and 7.7% for As, Cu, and Pb, respectively, present in a sample at 0.87 µg L⁻¹, 0.81 mg L⁻¹, and 38.9 µg L⁻¹ concentrations.

The proposed method was applied for the direct determination of As, Cu, and Pb in 12 Brazilian sugar cane spirits. The concentration of contaminants varied from 0.81–4.28 µg L⁻¹ As, 0.28–3.82 mg L⁻¹ Cu, and 0.82–518 µg L⁻¹ Pb. (Table III). Only three samples presented a lead content higher than 200 µg L⁻¹ Pb, the maximum established by the Brazilian Ministry of Agriculture, Livestock and Food

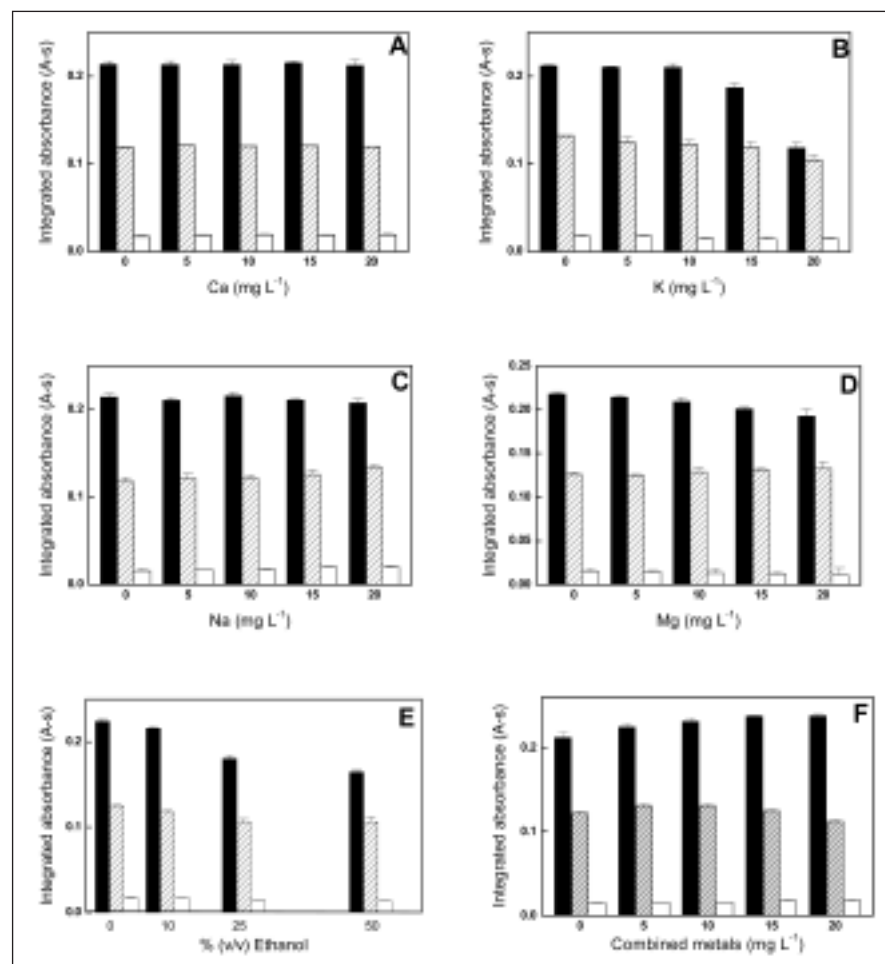


Fig. 2. Effect of variation of concentration (0–20 mg L⁻¹) of calcium (A), potassium (B), sodium (C), magnesium (D), ethanol (E) and combined metals in 25% (v/v) ethanol (F) on the absorbance of 20 µg L⁻¹ As (■), 20 µg L⁻¹ Pb (▨) and 100 µg L⁻¹ Cu (□) in 0.2 mol L⁻¹ HNO₃.

TABLE II
Slopes and Correlation Coefficients Obtained for As, Cu, and Pb in Different Matrices

Analytical Solutions	S (Slope)			R ² (Correlation Coefficient)		
	As	Cu	Pb	As	Cu	Pb
0.2% HNO ₃	0.02197	2.894E-4	0.00574	0.99981	0.99964	0.99989
Cachaça 1	0.02130	2.316E-4	0.00449	0.99867	0.99923	0.99924
Cachaça 2	0.02022	2.228E-4	0.00494	0.99964	0.99829	0.99943
Cachaça 3	0.01969	2.426E-4	0.00479	0.99895	0.99927	0.99715
Ethanol 10% (v/v)	0.01910	1.774E-4	0.00577	0.99938	0.99987	0.99930
Ethanol 25% (v/v)	0.01789	1.642E-4	0.00539	0.99980	0.99919	0.99914
Ethanol 50% (v/v)	0.01706	1.536E-4	0.00540	0.99902	0.99719	0.99860
5.0 mg L ⁻¹ Ca, Mg, Na, K	0.01725	2.412E-4	0.00520	0.99855	0.99914	0.99948
Ethanol 10% (v/v) plus 5.0 mg L ⁻¹ Ca, Mg, Na, K	0.02048	2.304E-4	0.00478	0.99980	0.99854	0.99778

TABLE III
Results for As, Cu, and Pb in Brazilian Sugar Cane Spirits (mean ± standard deviation) Using the Developed Procedure Without Sample Treatment and Recoveries (in %) for Spiked Spirit Samples

Sample	Concentration of Analytes			Recoveries (%)		
	As (µg L ⁻¹)	Cu (mg L ⁻¹)	Pb (µg L ⁻¹)	As	Cu	Pb
1	2.21 ± 0.04	2.05 ± 0.05	1.50 ± 0.13	97	110	96
2	0.961 ± 0.042	0.932 ± 0.042	44.3 ± 1.50	97	99	95
3	1.87 ± 0.08	0.220 ± 0.012	25.4 ± 0.78	101	111	101
4	4.28 ± 0.01	3.61 ± 0.11	518 ± 4.17	100	110	96
5	3.07 ± 0.16	1.82 ± 0.03	38.9 ± 1.99	97	99	98
6	3.26 ± 0.18	0.810 ± 0.011	0.820 ± 0.031	112	103	97
7	2.24 ± 0.08	1.20 ± 0.02	438 ± 5.26	94	104	103
8	0.960 ± 0.022	0.430 ± 0.010	216 ± 3.89	107	97	100
9	2.90 ± 0.14	2.78 ± 0.09	11.3 ± 0.34	95	98	94
10	0.873 ± 0.031	0.281 ± 0.011	2.04 ± 0.08	99	98	98
11	0.812 ± 0.011	3.82 ± 0.04	93.0 ± 4.18	101	100	101
12	1.24 ± 0.08	1.30 ± 0.02	49.8 ± 2.58	108	97	99

Supply (7). The levels of As, Cu, and Pb found in this work were close to those obtained for cachaça (0–3.0 µg L⁻¹ As, 0–3.64 mg L⁻¹ Cu, and 0–526.0 mg L⁻¹ Pb) reported in the literature (5,9,12,14).

Accuracy studies were also carried out using recovery experiments for cachaça samples spiked with 10 µg L⁻¹ As and Pb, and 100 µg L⁻¹ Cu. Recoveries for As, Cu, and Pb spikes were in the 94–112%,

97–111%, and 95–101% range, respectively. Calculated characteristic mass values (m_0 , in pg/0.0044 A.s) for As, Cu, and Pb were 16, 119, and 28, respectively. It is interesting to note that typical charac-

teristic mass values for single-element conditions for the THGA furnaces recommended by the manufacturer are 40, 17, and 30 pg (25). The value for As is 2.5-fold lower than that recommended in single-element condition and practically equal for Pb. It is important to emphasize that for copper the calculated characteristic mass in the proposed method was 11-fold higher when compared with the recommended value in single-element condition due to the less sensitive wavelength used.

CONCLUSION

This work presents a simple, fast, and accurate method for the direct and simultaneous determination of As, Cu, and Pb in sugar cane spirit (cachaça) samples by graphite furnace atomic absorption spectrometry. The recovery values of the spiked samples indicated that no sample treatment was necessary to accurately determine arsenic, copper, and lead in commercial sugar cane spirit samples. The limits of quantification obtained ($2.0 \mu\text{g L}^{-1}$ As, $40 \mu\text{g L}^{-1}$ Cu, and $1.2 \mu\text{g L}^{-1}$ Pb) exceeded the requirements according to the Brazilian Food Regulations (decree number 13 from the Brazilian Ministry of Agriculture, Livestock and Food Supply) which established the maximum permissible level for As, Cu, and Pb at 0.1 mg L^{-1} , 5 mg L^{-1} and 0.2 mg L^{-1} , respectively, in cachaça. With the proposed method, around 15 measurements per hour can be performed. It is important to point out that the atomizer lifetime was limited by the durability of the external wall of the tube (the external wall usually deteriorates faster than the platform). For comparison purposes, the lifetime of the graphite tube used in the direct determination of As, Cu, Fe, Mn, and Ni in fuel ethanol (alcoholic

matrix), employing palladium plus magnesium as the modifier, was equivalent to 250 firings (23).

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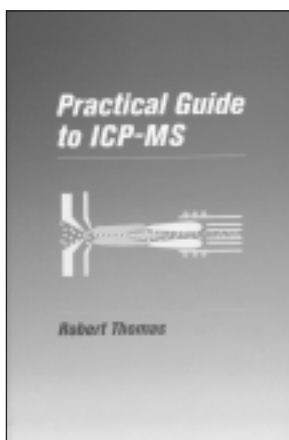
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